

Quantum Physics In America Between the Wars

Development of the Wigner-Seitz method for interpreting metallic structure, study of Brillouin zones and calculations of energy bands in solids led to new understanding of molecular theory and of electronic structure in crystals.

by John C. Slater

MANY YOUNGER PHYSICISTS feel that all physics has grown up since World War II; or if they admit some earlier science, they feel that in this country everything started with the influx of European scientists as a result of political difficulties, beginning with the rise of Hitler in 1933, in Germany and Italy.

I believe this idea is a misconception. I would like to describe the June 1933 Chicago meeting of the American Physical Society. It was a gathering in which the shift of emphasis from European to US physics was clearly evident. I will give an account of the physics climate in the US during the 1920's and 1930's as eminent European scientists joined the increasing number of US-trained physicists on our campuses. I will also describe the quantum-physics and molecular theory when Harvard and Princeton stood out as two prime centers of activity. Finally, by means of a review article on electronic structure of metals that I published in 1934 in *Reviews of Modern Physics*, I will present a survey of solid-state theory at the time.

Chicago meeting

Numerous foreign speakers were brought over for the meeting: Frederick Aston, the isotope man from Cam-

bridge, John Cockcroft from England, Niels Bohr from Copenhagen, Enrico Fermi from Rome, as well as several mathematicians, meteorologists and representatives of other sciences. It was an extraordinary meeting in that some of the sessions were held on the grounds of the world's fair. With typical world's fair architecture, a round lecture room had been designed with acoustics so bad that a public-address system was absolutely imperative and with such limited seating capacity that a large part of the audience had to stand around the circumference. Nobody who was there will ever forget poor Bohr's lecture. Those who knew him will realize that he was almost entirely inaudible even to people in the same room, and yet he was not very adept at public-address systems. As he went to and from the blackboard, he kept rotating in the same direction, winding himself up in the cord of his lapel microphone like a mummy. He set the system howling, had to be unwound by helpers from the audience, and generally provided enough amusement to help the audience (which included mothers with their children as well as physicists) forget that even with electronic equipment, they could hardly hear a word he said.

Most of the sessions, however, were held under normal surroundings at the

university, and they were inspiring sessions. The thing that impressed me—very consciously, as I look back—was not so much the excellence of the invited speakers as the fact that the younger American workers on the program gave talks of such high quality on research of such importance, that for the first time the European physicists present were here to learn as much as to instruct. One must remember that in the 1920's the first thing required of a young American graduate student of physics was to learn German so he could follow the new work in the field. Today the first



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thing a young physicist of continental Europe does is learn English so he can attend meetings and learn of new progress. This trend was already becoming visible in the 1930's, and I felt the tide turning more specifically at this 1933 Physical Society meeting than at any other one moment.

Quantum physics in 20's and 30's

This thought suggests, therefore, that instead of going over the history of the period between the two world wars in chronological fashion, I adopt one of the tricks of the chronicler: fix on a particular instant (in this case 1933) and ask what the situation of quantum physics in America looked like at that moment. We must remember that the summer of 1933 was a rather dramatic and momentous time. The inauguration of Franklin Roosevelt as president in the preceding spring, the previous breakdown of the banks and the "hundred days" that had ushered in the New Deal constituted an unusual era of American life. It was also when Hitler was taking over in Germany. Both of these episodes were in a way a result of the long depression that had been going on since 1929, following the fabulous decade of the roaring twenties. At this point it is probably worthwhile to sneak in another of the tricks of the chronicler, the flashback. How did the twenties treat quantum physics, both in America and throughout the world?

That was an extraordinarily interesting period. It was one of the most constructive decades that the country has known. Money was flowing freely, and the rebuilding of the cities that went on then put them into the shape that they have maintained until the last two decades, again a great period of construction. The universities received enormous benefactions, made remarkable growth, and reached the form in which many of them remained until recent years of still more remarkable development. It was a time of relaxed international feeling, of very active interchange between people of different countries.

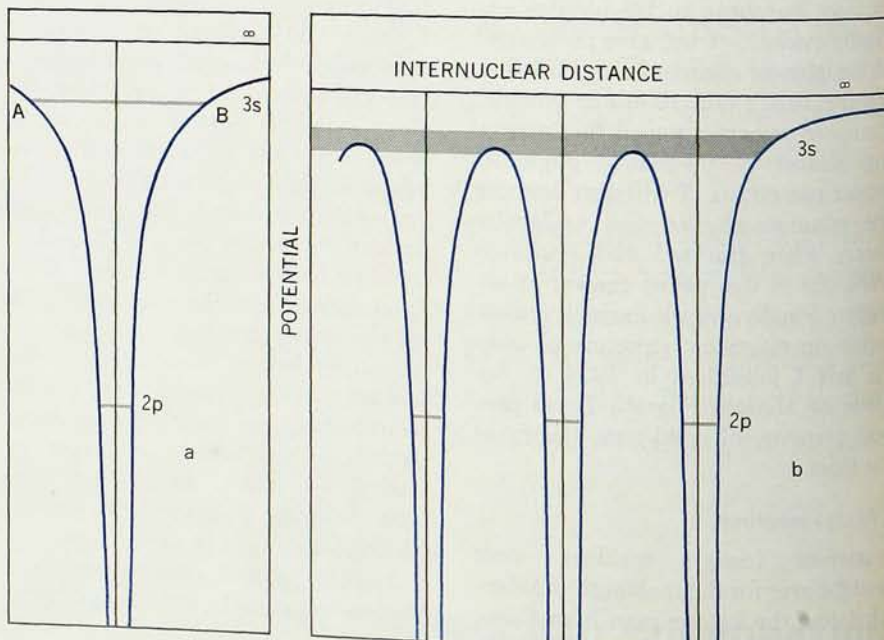
This was the decade in which the quantum theory really grew up, probably the most fruitful decade which the science of physics has ever known. The physics student starting his career in 1920 as I did (I became a graduate

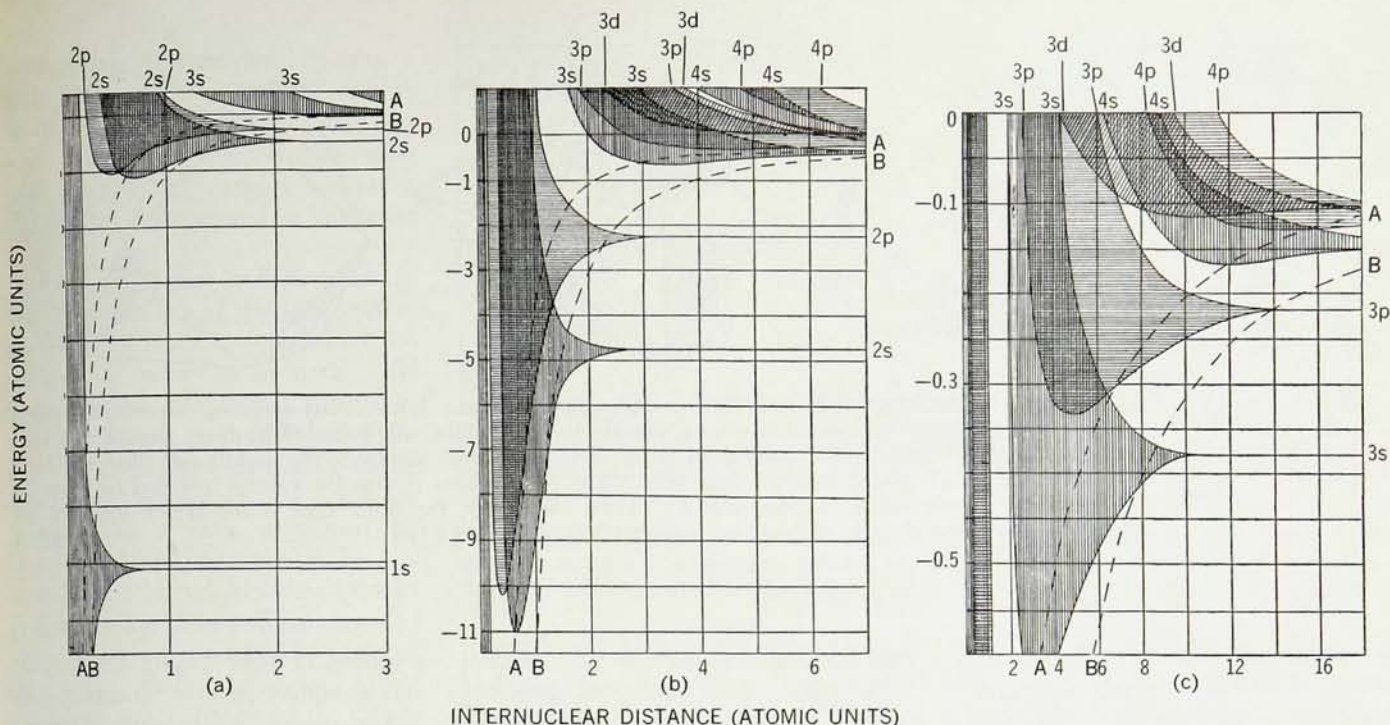
student at Harvard that year) looked up to a group of distinguished older leaders: men like Max Planck, Albert Einstein, Bohr, Max von Laue, Lawrence Bragg, Max Born, Peter Debye, Leon Brillouin, Paul Ewald, Charles Darwin, Arnold Sommerfeld and Erwin Schrödinger, all of whom were well established by 1920. But during the 1920's a great rush of new physicists entered the field. Among the theorists, arranged alphabetically, were Hans Bethe, Felix Bloch, Gregory Breit, Louis de Broglie, Edward Condon, Paul A. M. Dirac, Carl Eckart, Fermi, Frenkel, Samuel Goudsmit, Otto Halpern, Douglas Hartree, Werner Heisenberg, Walter Heitler, William Houston, Erich Hückel, Friedrich Hund, Egil Hylleraas, Pascual Jordan, Oskar Klein, Hans Kramers, Ralph Kronig, Lev Landau, Otto Laporte, John Lennard-Jones, Fritz London, Philip Morse, Nevill Mott, Robert Mulliken, John von Neumann, Lothar Nordheim, Robert Oppenheimer, Wolfgang Pauli, Linus Pauling, Rudolf Peierls, Giulio Racah, Leon Rosenfeld, Svein Rosseland, John Slater, Edmund Stoner, Igor Tamm, Llewellyn Thomas, George Uhlenbeck, A. Unsöld, John Van Vleck, Ivar Waller, Gregor Wentzel, Eugene Wigner, and Clarence

Zener. This list could easily be doubled to include other important names in the field.

Those of us who started our careers at that particular time found ourselves probably in the most competitive situation that has even been seen in physical science. Here was the decade in which the most momentous physics discoveries in a century were being made, and here were 50 or more ambitious young men, entering a field with a much smaller number of older and very distinguished workers, all trying to be in on the exciting discoveries that all were convinced were going to be made. The inevitable result of this effort was a great deal of duplication. Almost every idea occurred to several people simultaneously. No one had time to follow through a line of work without having someone else break in on his developments before they were finished. It is probable that any one of a dozen theoretical physicists whom I have mentioned, given the situation that faced physics in 1924 just before the development of quantum mechanics, would have worked out its principles eventually, had he been free to take his time about it. But as things were, no one had the time to do it all by himself, and wave

POTENTIAL ENERGY affecting an electron in a self-consistent model of a sodium atom (a). For sodium crystal (b): There are maxima of potential between atoms. Shaded area indicates broadened 3s level. Potentials are adjusted so that x-ray levels agree and go from minus infinity at the nucleus to zero at infinity. —FIG. 1

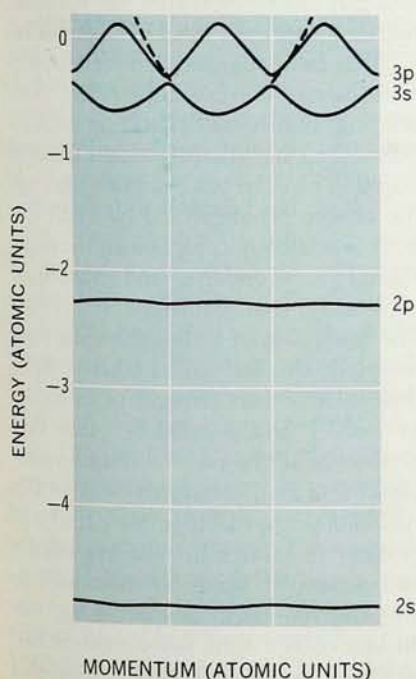




ENERGY DEPENDENCE on internuclear distance for sodium (in atomic units). Dotted curve A represents maximum potential energy at the edge of the cell, and B represents mean potential energy throughout the cell. No broadening or shifting of energy occurs for the 1s, 2s and 2p levels (a). Lower energy levels are occupied by electrons; the upper ones are empty. Only the lower half of the 3s band (c) is occupied. —FIG. 2

mechanics is a composite of the work of many men. Certainly it attained a richness and variety of approach in this way that it would never have had

MOMENTUM EFFECT for energy. 2s and 2p energies are relatively unaffected, but 3s and 3p levels are strongly dependent on wave vector k . —FIG. 3



if it had been the work of one or a few isolated scientists.

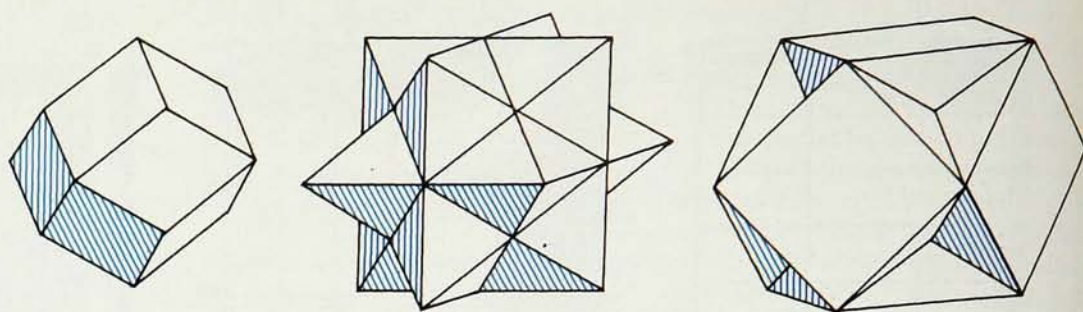
One will realize that Americans were well represented in the list I have given. Breit, Condon, Eckart, Houston, Morse, Mulliken, Oppenheimer, Pauling, Slater, Van Vleck, and Zener almost all originated in this country, and all received their training here. By 1933, a number of others had moved here—a result of superior opportunities in the US rather than of European intolerance. These men include Goudsmit, Halpern, Laporte, von Neumann, Thomas, Uhlenbeck and Wigner, most of whom were in the country well before 1933. Others, including Bethe, Bloch, Fermi, London and Nordheim, came somewhat later but well before the end of the 1930's. Still others came later. When we survey American quantum physics in 1933, we naturally wish to consider the state of progress of those who were then living in this country.

Centers of development

Probably the most active center in quantum theory during the 1920's, was Harvard. Out of the list that I gave in the preceding paragraph, there were four who had received much of their

training there, namely Oppenheimer, myself, Van Vleck and Zener; two more, Breit and Mulliken, had spent extensive postdoctoral periods at Harvard. There was a distinguished group of faculty members interested in the development of the quantum theory. Theodore Lyman was the discoverer of the fundamental series in the hydrogen spectrum that bears his name. Frederick Saunders collaborated with Henry Russell of Princeton in unraveling the calcium spectrum, which led to the Russell-Saunders coupling theory. William Duane had been active in x-ray methods to verify quantum principles, and Percy Bridgman, though his main interests were on the experimental side, had a deep interest in all aspects of the theory of solids. Edwin Hall, of the Hall effect, was still active. The course on quantum theory, an excellent one and one of the first in this country, was given by Edwin Kemble, whose major interest was molecular spectrum theory.

Perhaps the next most active center was Princeton, where Karl T. Compton, though not a theorist himself, had assembled a strong group before he left in 1930 to become president of MIT. Wigner had joined the faculty



ZONES IN MOMENTUM SPACE for body-centered space lattice, face-centered momentum lattice. First solid represents the middle zone, identical with middle cell, bounded by faces parallel to (110) planes. The second solid consists of parts of a polyhedron similar to the middle cell (first solid) cut into pieces and pasted onto the first solid. The second zone is then the volume included between the first and second solids, also bounded by (110). Similarly, the third zone is the region included between the second and third solids, bounded by (110) and (100). —FIG. 4

in 1930, and Condon, Eckart and Morse, as well as many others, received their advanced training there. Condon remained on the staff for a number of years. Chicago, where Arthur H. Compton had been for some time before 1933, had Mulliken among its students and Eckart on its staff. California Institute of Technology, recently

vitalized by the addition of Millikan and others, had numbered Pauling among its graduates and had Houston on its staff. Michigan had been greatly strengthened by the group under Goudsmit, Laporte and Uhlenbeck. These universities, and many others, were actively preparing students in quantum theory during the 1920's, and by the early 1930's (so I believed) the American physics departments were giving better training in quantum theory than their European counterparts.

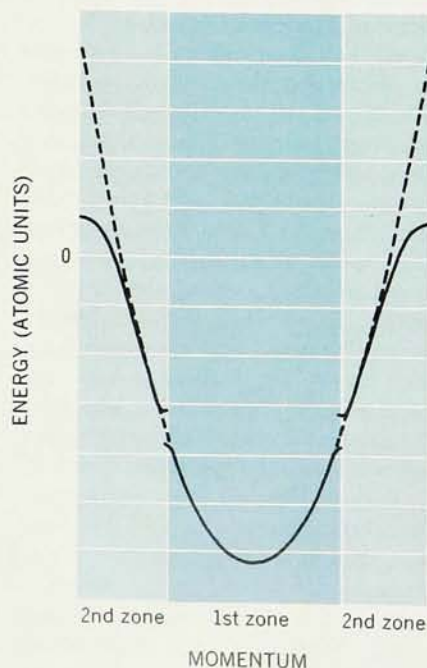
Atoms, molecules and quanta

This account is enough to set the stage for the story of quantum physics in 1933. First let us think of fundamental quantum mechanics and of the practically inseparable problem of atomic theory. Here of course one thinks of the great European workers: Bohr, Sommerfeld, Heisenberg, Dirac, de Broglie, Born, Pauli, Schrödinger and many others. This development was practically complete by the end of the 1920's. But we must not think that even in this early and largely European development American physicists were unimportant. We must not forget that the greatest impetus toward the understanding of the interrelation between waves and particles came from the Compton effect, discovered by A. H. Compton in 1923. Its implications were thoroughly understood by him, and in the atmosphere of Harvard in 1923, where Van Vleck, Breit and I were all actively working, we had a very lively understanding of the probability that a new

synthesis of light quanta or photons, and stationary states or quantum conditions, must be on the way. We were all ready for quantum mechanics when it came and had played our part in bringing it about though competition was so keen in those days that no one person could go very far without running into the work of others.

By 1927 quantum mechanics was essentially complete, but its application to atomic structure was not, though Dirac's explanation of the spinning electron carried things a long way. In 1929 I suggested determinantal functions composed of spin orbitals—which combined ideas that Dirac, Heisenberg, Pauli and Hund had developed several years earlier—and put multiplet theory for nonrelativistic atoms on a useable basis. Also in 1929 Breit suggested the relativistic Hamiltonian that has been so useful in treating relativistic effects in atoms. Condon, along with his student George Shortley at Princeton, at once took up the atomic problem, and by 1933 the work was mostly complete and was included in Condon's and Shortley's book that was published in 1935.¹ The other side of atomic theory is represented by the self-consistent field that Hartree had thought of in 1928. In 1930 I had pointed out that this method could be derived from a variational scheme, leading the way to the variational approach to analytical approximations for self-consistent atomic and molecular wave functions and to the Hartree-Fock method. By the middle 1930's some self-consistent calculations were being done in this

JOINING OF ENERGY FUNCTIONS from neighboring periodic regions. Energy is a function of momentum from different momentum zones. The segments pieced together approximate a parabola (dashed curve) but with an energy gap at the boundary between zones. —FIG. 5

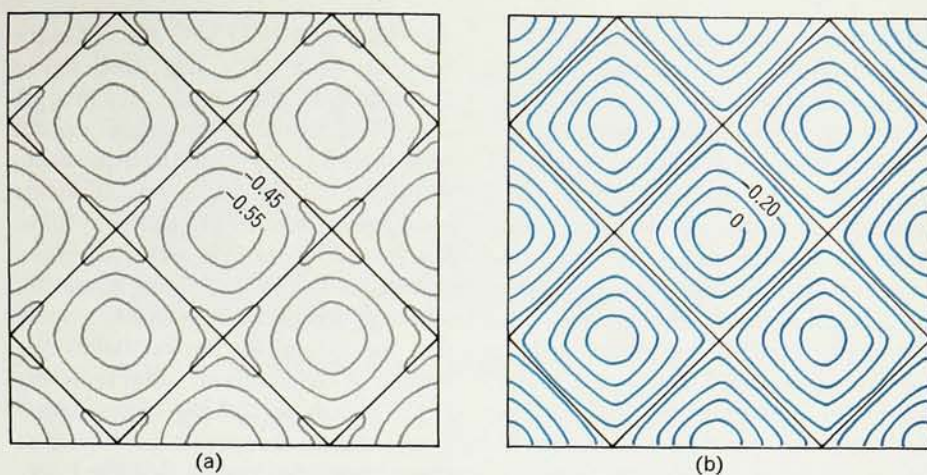


country, and Hartree had become a fairly frequent visitor to MIT, where by then I was department head and where he liked to use the differential analyzer, the large analog computer that was being developed by Vannevar Bush.

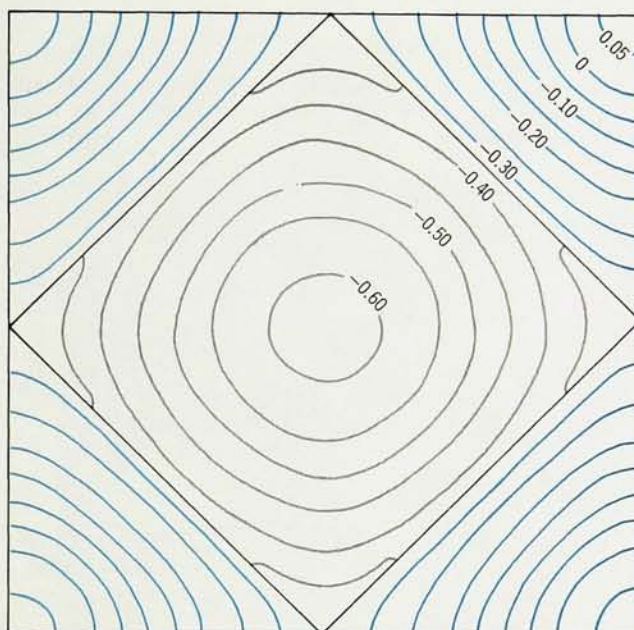
Molecular theory had its start in two developments of the late 1920's: the Heitler-London method and the method of molecular orbitals. Of these, the first was carried further in the early 1930's by myself and Pauling, who emphasized its relation to the directional properties of valence bonds. The second, developed by Hund and Mulliken, was already well established (through Mulliken's work) in America by 1933 and was proving valuable for interpretation of molecular spectra. Hubert James and Albert Coolidge's classical work on the theory of the hydrogen molecule—the first really accurate calculation of a molecular structure—was completed at Harvard under Kemble's direction in 1933. At the same 1933 Chicago meeting of the American Physical Society, there was a symposium on quantum theory as applied to molecules. Mulliken, Pauling, Henry Eyring and I spoke on topics that would sound very up-to-date to a modern specialist.

Wigner-Seitz method

The topic that I now wish to follow with particular care is the development, in America, of the theory of electronic structure of crystals. 1933 is also memorable for the Wigner-Seitz method for discussing metallic theory, worked out at Princeton. The general ideas of the motion of electrons in the type of periodic potential that one finds in a crystal had been worked out by Bloch and Bethe in 1928, and by 1930 Brillouin and Morse had made significant advances in the theory. The methods of Bloch, Bethe and Brillouin had shown us the general type of theory to be used and had led to an understanding of the relations between energy bands, energy gaps and so on, and the differences between insulators, semiconductors and metals. But they were poorly adapted for quantitative calculations of actual crystalline energy bands and wave functions. The free-electron type of theory had been worked out in 1928 by Sommerfeld and his students



TWO DIMENSIONAL VARIATION of energy. Brillouin zones cut by a plane yield energy contours in momentum space. (a) Energy band going to 3s at infinite separation. (b) Energy band going to 3p at infinite separation. —FIG. 6



ENERGY CONTOURS showing two zones. —FIG. 7

—a group including Houston and Eckart, who were postdoctoral workers in Munich—but it was realized that one had to understand the energy bands to proceed with the treatment of different crystal types.

This situation was changed immediately by the much more powerful method of Wigner and Seitz, the cellular method, that dominated the field for the rest of the 1930's. By the time of the 1933 Physical Society meeting, I was already using this method for investigations into the energy bands of sodium and was starting work on a review article on the electronic structure of metals, which appeared in the

Reviews of Modern Physics in 1934.² Since this article furnishes a survey of the progress of solid-state theory in the period we are speaking of, I shall make it the basis of my treatment. To make it clear that we are talking about the 1930's, I shall reproduce some of the figures from that review article to illustrate what I shall say about the theory.

In figure 1 we see first the potential energy affecting an electron in a self-consistent model of a sodium atom. The potential energy goes to minus infinity at the nucleus, to zero at infinity. In figure 1a, we show the positions of the 2p and 3s energy levels of sodium,

the 3s being the easily detached valence electron. If atoms are brought together to form a sodium crystal, we have the potential shown in figure 1b, in which there are maxima of potential energy between the atoms, with the potential rising to a higher asymptotic value at infinite distance from the boundary of the crystal. As the atoms are brought together, the 2p level, far within the atom, is not modified, but the 3s level is broadened into a band and lowered; the lowering leads to the binding of the atoms to form the crystal.

This broadening and modification of the energy levels, shown in figure 2, is the result of calculations that I was

working on in 1933 with the Wigner-Seitz method. The first part, figure 2a, illustrates that at the distance of separation found in the actual crystal (between 3.5 and 4 units on the scale of the figure) the 1s, 2s and 2p levels have not broadened or shifted at all in energy. This fact is depicted more clearly for the 2s and 2p in figure 2b, although figure 2c is on such a scale that the 2s and 2p lies far below the bottom of the diagram. The broadening of the 3s and of the higher levels is well shown, however. In the actual crystal, we must realize that the lower energy levels are occupied by electrons; the upper ones are empty. Specifically, the 1s, 2s and 2p are oc-

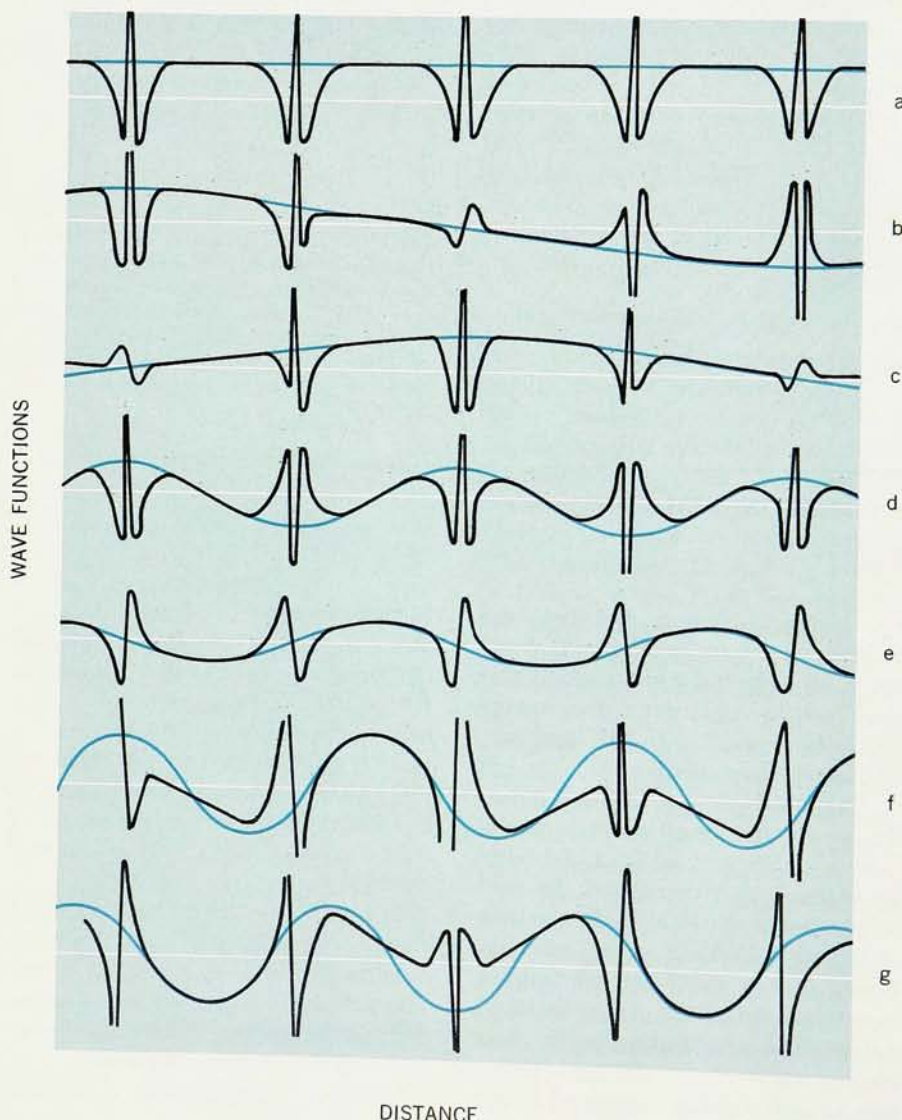
cupied; the 3s is half occupied; higher ones are empty. Only the lower half of the 3s band, shown in figure 2c, is occupied, which is indicated in figure 1b as the lowering of the band in the crystal as compared with the atom. The higher levels in figure 2c are empty levels. The optical properties of metallic sodium arise from the excitation of electrons from the lower, occupied bands to the upper empty ones.

Brillouin zones

There is more information in the energy bands than one sees from figure 2. Bloch had proved that each wave function in a periodic structure like a crystal can be written in the form of a plane wave, expressed in complex exponential form as $\exp(i\mathbf{k}\cdot\mathbf{r})$ ($\mathbf{k}$ is a wave vector pointing along the wave normal, of magnitude 2π divided by the wavelength, and $\mathbf{r}$ is the radius vector) multiplied by a periodic function of position repeating in each unit cell of the crystal. The reason for the splitting of the wave functions into the energy bands is that those functions with different wave vectors $\mathbf{k}$ have different energies. It is then interesting to plot the energy as a function of $\mathbf{k}$. Figure 3 is such a plot, in which $\mathbf{k}$ is along a particular direction, in this case the (110) direction, and in which we give the energy as a function of the magnitude of $\mathbf{k}$. We see the practical constancy of the 2s and 2p energies (showing that their energies are not appreciably split into a band), whereas the 3s and 3p levels show a strong dependence on $\mathbf{k}$. We also note another interesting point: The figure is periodic in the $\mathbf{k}$ space. The central repeating region is called the central Brillouin zone, and all information about the energy bands can be given by studying only this central Brillouin zone.

The Brillouin zone is really a three-dimensional thing and is shown in the first polyhedron of figure 4. There is a good reason for taking part of the energy as a function of $\mathbf{k}$ from the central zone, part from one of the neighboring periodic regions, and joining these as if they were parts of a single curve. Thus, in figure 5, we show the 3s and 3p functions, from figure 3, joined up in such a way. We see that the different segments of the resulting curve follow rather closely

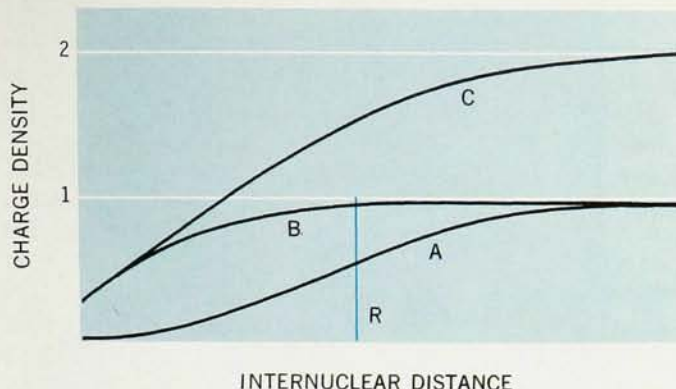
WAVE FUNCTIONS of the 3s band as a function of position going through the crystal from one atom to its nearest neighbor. The various curves show values of $\mathbf{k}$, from $\mathbf{k} = 0$, in a, to the edge of the Brillouin zone for g. —FIG. 8



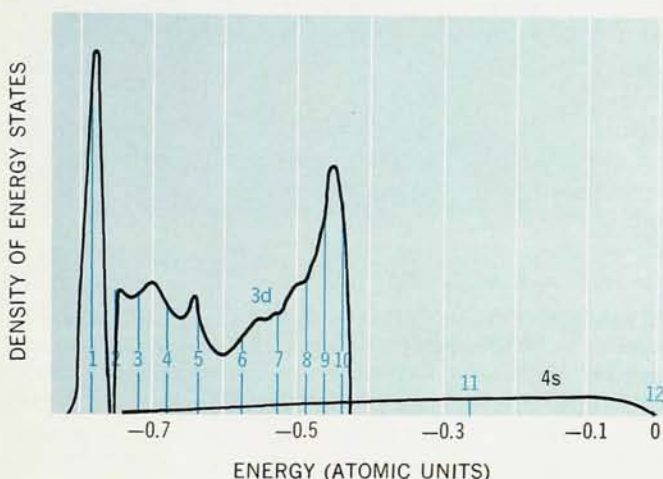
the parabola that is illustrated by the dashed curve but with an energy gap in which we go from one zone to the next. This dashed curve has a simple significance. The wave vector k is closely related to the momentum: If we have a free electron, so that its wave function is just the exponential $\exp(i\mathbf{k}\cdot\mathbf{r})$, we can demonstrate by de Broglie's relation that its momentum is $\hbar k$. Its kinetic energy would be $mv^2/2$, where m is the mass and v the velocity, or $(mv)^2/2m$. Since mv is the momentum, the energy is $k^2\hbar^2/2m$. This expression, if plotted as a function of k , yields a parabola such as that in figure 5. In other words, the free-electron energy is a good approximation to the energy of the electron in the energy band.

We can show this approximate free-electron nature of the energy bands in three dimensions. What is called the second zone in figure 5 consists in three dimensions of parts of a polyhedron like the Brillouin zone of figure 4, cut up into pieces and plastered onto the faces of the first polyhedron. This forms the second polyhedron of figure 4. Similarly we can have a third zone, including those regions between the second and third polyhedra of figure 4. Brillouin had made a fascinating study of these zones and their geometry in 1930. Now we can cut through such a figure with a plane, not just with a line as we did in figure 3 and figure 5, and can ask about the values of the energy at points in this plane. This can be indicated by a set of contour lines, giving lines of constant energy. In figure 6 we find such energy contours for the 3s and 3p bands of sodium, depicting the two-dimensional variation of the energy as figure 3 depicted its variation in one dimension. And in figure 7 we show these pieced together as we did in a one-dimensional case in figure 5.

If we had the free-electron case, leading to the parabola in figure 5, in an xy plane the energy would be given by setting $(k_x^2 + k_y^2)\hbar^2/2m = \text{energy} = \text{constant}$, which is the equation of a circle. We see from figure 7 that the lower energies correspond to circles, but for higher energies the circles become very distorted, particularly as they approach the boundaries of the zone. However, the occupied energy



SPIN EFFECTS. Density of electrons around a given electron plotted against internuclear distance. Curve A for electrons of same spin as given electron, B of opposite spin, C for both spins combined. One unit of density represents maximum allowable value for electron of one spin. —FIG. 9



DENSITY OF ENERGY STATES for copper. Number of levels per unit of energy as a function of energy. Vertical lines indicate portion of bands filled by 1, 2, . . . 12 electrons. —FIG. 10

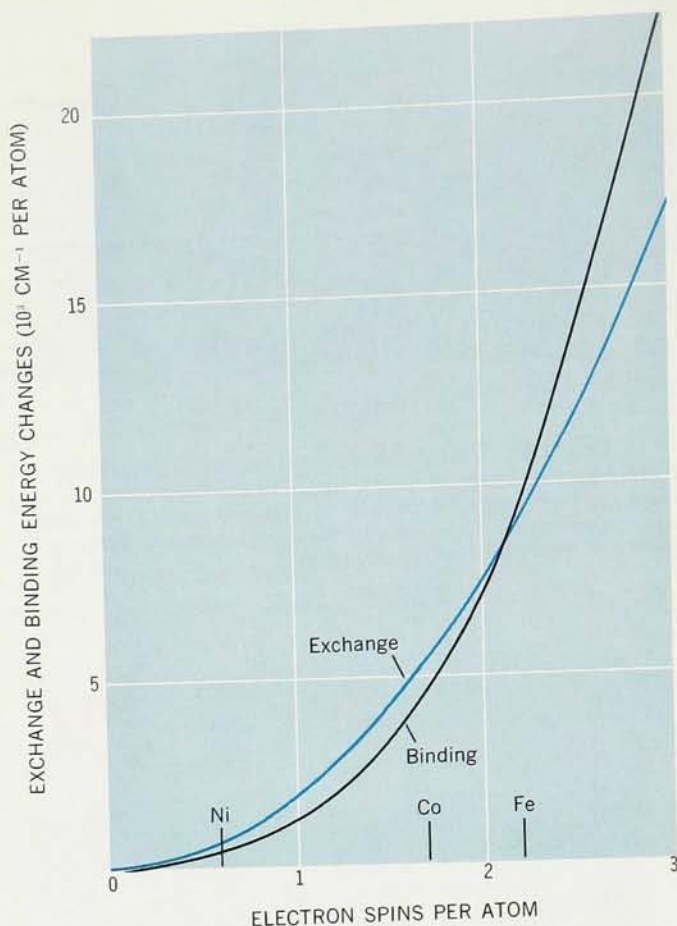
levels (those below the so-called Fermi energy) correspond to the circles well within the central zone. For the Fermi energy the surface of constant energy (in three dimensions), called the Fermi surface, is very nearly a sphere. Thus for the occupied energy levels of sodium, the free-electron approximation holds quite accurately.

Wave functions

This does not mean at all, however, that the wave functions of the electrons are plane waves, as they would be for free electrons. This is illustrated in figure 8, in which we show the wave function of the 3s band as a function of position as we go through

the crystal, along a line from one atom to its nearest neighbor. The various parts of this figure, a . . . g, show different values of the magnitude of k , from $k = 0$ for a to the edge of the Brillouin zone for g. In each case the wave function goes through rapid oscillations near the nucleus. These are similar to the behavior of an atomic 3s or 3p wave function in the isolated sodium atom. Between the nuclei, however, the wave functions run smoothly, not far from the dashed curves that represent the real part of the exponential plane wave.

We were interested in 1933 not only in solving Schrödinger's equation for the type of periodic potential found in



EXCHANGE AND BINDING energy changes between ferromagnetic and nonferromagnetic states as a function of electron spins per atom. For ferromagnetism exchange energy term must be greater than the binding energy term. —FIG. 11

a metal, but also in the determination of this potential from the electronic wave functions. It was known from the Hartree-Fock method that we could arrive at this determination by taking the potential of all nuclei, of the charge distribution of all electrons (including the one whose motion was being investigated), and then making an exchange correction to account for the fact that this electron really did not act electrostatically on itself. The nature of this exchange was elucidated in the paper of Wigner and Seitz. They noted that an electron, because of the Pauli exclusion principle, keeps other electrons of the same spin out of a region, roughly a sphere and large enough to contain one electron of the same spin. In other words, if one goes out from an electron, the probability of finding another electron of the same spin infinitely close to the electron in question is zero, and it gradually rises

to the limiting value at a distance equal to the radius of this sphere, called the Fermi hole, on account of its relation to Fermi statistics. In curve A of figure 9 we see how the probability of finding another electron of the same spin rises as r increases. This curve is computed for a free-electron gas, for which simple calculations can be made, as Wigner and Seitz did, rather than for the situation actually existing in the metal.

Exchange effects

The exchange integral is the electrostatic interaction of the electron with the deficiency of electronic charge located within the Fermi hole. Because of its existence, there is an energy preference for a situation in which two electrons are found with parallel spins, rather than with antiparallel spins. The reason is that an electron is not nearly as effective in

keeping an electron of opposite spin away from itself as one of the same spin. The Pauli principle does not operate, and the other electron is kept away only by electrostatics. The details of this electrostatic repulsion, leading to what is known as the correlation effect, were well known from studies of the helium atom, by Hylleraas, myself and others around 1928: A problem in which the interaction of two electrons that have opposite spin was investigated in detail. From this study the distribution of electrons of opposite spin around a given electron is known to be of the nature shown in figure 9, curve B. The study of the exchange and correlation effects in the sodium crystal had been carried out by Wigner and Seitz in their 1933 paper and applied to the study of the cohesive energy of the crystal, with very satisfactory results.

Since two electrons of opposite spin orientation can approach closer than those of the same spin and since electrons repel electrostatically, this means that the energy of a state with opposite spins tends to be higher than that with parallel spins. This fact had been understood since Heisenberg's fundamental work in 1926. The most straightforward application of it was in Hund's rule that stated that the triplet energies in a two-electron atom, in which the spins of the two electrons are parallel with each other, lay below the singlet, in which the spins were opposite. But Heisenberg had also suggested that this was the explanation of the phenomenon of ferromagnetism that arose because the spins of all the magnetic atoms in a magnetized crystal of iron, cobalt or nickel tended to lie parallel to each other.

Theories of magnetism

Heisenberg's idea had led to a great development in magnetism. Van Vleck, in particular, had taken up this subject with great enthusiasm, and in 1932 his classic book on electric and magnetic susceptibilities had come out, laying the foundation for all subsequent work on magnetism, both in America and elsewhere. The approach that he and Heisenberg had used, however, was based on the assumption of an exchange integral acting between magnetic atoms and measuring their tendency to orient paral-

lel to each other. There was little progress at the time (and in fact there has been little progress since then) in computing these integrals from first principles and even in explaining why magnetism is found in the elements that show it.

Bloch had taken quite a different approach to magnetic problems with the energy-band method. He had asked whether a metal, described in terms of energy bands, could reduce its energy by being magnetized. In the ground state of the crystal, energy bands are filled (with an electron of each spin in each state) up to the Fermi energy. If the crystal were to magnetize, electrons with spin down would have to be removed from the top of the occupied energy levels. They would have to reverse their spins to have spin up and then because of the Pauli principle would have to go to higher energy levels not already occupied by electrons of spin up. For two reasons the energy would change in this process. It would increase by an amount that would be greater, the broader the energy band, because electrons are being excited to higher levels; it would decrease because of exchange since, as indicated in figure 9, in the magnetized state other electrons would keep away from a given electron more effectively than in the unmagnetized state. Bloch had made calculations for a free-electron metal, in which the energy was given by the same expression $k^2\hbar^2/2m$ that was mentioned earlier, and in which the exchange effect could be calculated. He had shown that such a metal would not spontaneously magnetize. The energy increase was too great because of the width of the energy bands.

Energy band approach

It had appeared to me for some time before 1933 that this energy-band theory gave the possibility of understanding ferromagnetism, whereas Heisenberg's and Van Vleck's approach could not deal quantitatively with it. Everyone assumed that in such metals as iron, cobalt and nickel the energy bands arising from the 3d electrons would be much narrower than those arising from outer electrons. This condition is natural by analogy with figure 2, in which the inner electrons of an atom have wave functions

that do not overlap and consequently energy bands that do not broaden until we reach much smaller interatomic distances than we find in the crystal. For this reason the 3d orbital in an iron-group atom is small enough so that we should have small broadening. In 1930 I had estimated the sizes of various shells in the atoms and had shown that this supposition was verified. One should expect, then, that in a ferromagnetic metal the partially filled 3d band of electrons would require small enough energy increase when the electrons were lined up parallel to each other; thus the exchange effect, which could be estimated from atomic spectra, would outweigh it and lead to spontaneous magnetization.

I had been anxious to test this hypothesis quantitatively, and when the work of 1933 and 1934 showed that one could reliably calculate the energy bands by the Wigner-Seitz cellular method, I felt that the time had come to try to calculate the energy bands of a ferromagnetic crystal. Fortunately I had several graduate students who were interested in using the new methods to find energy bands. One of them, Harry Krutter, undertook to find the energy bands of copper, the next element beyond nickel, which would be expected to show the same type of 3d bands as the ferromagnetic elements. By 1935 he had found good energy bands and a density of states that showed, as one would suppose, that the band was quite narrow or that the number of states per unit energy range was very large.

In 1936 I applied these calculations to the ferromagnetic problem. In figure 10 we have the curve for density of states that was found in this way. The very high peak represents the 3d band, superposed on the much lower conduction band. In figure 11 there is a curve taken from the same paper, showing the magnitude of the increase of energy as a result of raising electrons to higher states and the decrease of energy on account of exchange, as a function of the number of missing electrons in the 3d band. This curve shows that the exchange effect predominates so that the metal would magnetize spontaneously for just the numbers of missing electrons found in iron, cobalt and nickel, thus verifying

the magnetic properties of these elements. Although the finer details of this calculation are not very reliable, recent calculations along the same line have demonstrated the essential correctness of this picture of ferromagnetism.

Crystal properties explained

Naturally these results on energy bands were encouraging enough to create a lot of activity in finding energy bands for many types of substances. Various students and colleagues of mine made calculations during the remaining 1930's on other metals, covalently bonded insulators like diamond and ionic crystals like KCl. In each case the energy bands were of the type required to explain the known properties (electrical, magnetic and optical) of the substance. Work along these lines went on at Princeton, and under my direction at MIT. Hund, in Germany, took up the method, and he and his students made valuable contributions. This energy-band work in the latter 1930's represents the first serious attempt to understand the electronic properties of real crystals in terms of calculations from first principles.

In spite of the success of these calculations, we realized that they were not perfect. The misgivings about the method were serious enough, however, so that it seemed desirable to improve it. In 1937 I suggested one way of doing this, which has now come to be called the augmented plane-wave method. In 1940 Conyers Herring, who had recently finished his doctoral work at Princeton and was carrying on postdoctoral work at MIT, suggested another method, the orthogonalized plane-wave method. Both of these methods were tested in the prewar period, the augmented plane-wave method by Marvin Chodorow on copper, the orthogonalized plane-wave method by Herring and Albert Hill on beryllium. But war was with us; further use of these methods had to be postponed to a later date.

References

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