

III. SOLID STATE PHYSICS

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A. EXTENSION OF THE ENERGY BAND THEORY

Advances have been made in several directions toward more accurate energy band calculations, as outlined in the Quarterly Progress Report, July 15, 1950, pp. 17-22.

1) The calculations of Mr. Pratt on Cu^+ by the simplified Hartree method are nearly complete. Tentative energy values are given in the table below:

Table of computed Cu^+ energies (Rydbergs)

Electron	Hartree	Hartree-Fock	Pratt	Exp.
1s	658.0	658.4	644.0	661.6
2s	78.45	82.30	75.5	81.0
2p	69.86	71.83	71.35	68.9
3s	8.968	10.651	9.75	8.9
3p	6.078	7.279	7.08	5.7
3d	1.195	1.613	2.00	1.50

Pratt's values show a tendency to be below the Hartree or Hartree-Fock values for s electrons, between them for p electrons, above for d electrons; the reasons for this can be understood in terms of the approximations involved. Agreement with experiment is good enough, in view of the simplicity of the method, as compared to either the Hartree or the Hartree-Fock method, to warrant an extensive program of calculation of atomic wave functions by this scheme.

2) Mr. Parmenter has started work on an extension of a scheme suggested by the writer in 1937 for calculating the energy bands in a metallic crystal. He has made a notable simplification of this method, and it should now provide a usable scheme, when combined with the simplified Hartree method of finding the self-consistent field, mentioned in 1), for making numerical calculations of energy bands.

3) Mr. Meckler has started a program of calculating the multiplet structure in the oxygen molecule. This problem was suggested to him by the writer for the following reason. Either the Heitler-London or the energy band theory of ferromagnetism, as ordinarily used, represents a first-order calculation; the Heitler-London method is appropriate for widely separated atoms, the energy band method for condensed systems. For more accurate results holding at intermediate distances, either of these methods should be made the basis of a perturbation calculation which would then hold at all distances. The oxygen molecule furnishes the simplest problem analogous to what we meet

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in the intermediate case: the ground state of the molecule is a triplet (analogous to the ferromagnetic state of a solid), and the ground state of the separated atoms is likewise a triplet (as with paramagnetic atoms). The perturbation problem is not too hard to solve completely, though this has not been done in previous chemical treatments of the oxygen problem. Meckler hopes to carry out such a solution, comparing Heitler-London and molecular orbital methods as starting points. We hope that the results will give insight into the related but much more complicated ferromagnetic-paramagnetic problem, including such interesting questions as that of magnetite mentioned in the July Progress Report.

J. C. Slater

B. SELF-CONSISTENT CALCULATIONS FOR Cr^+ AND Cu^+

All six wave functions have been obtained from the solutions of Schrödinger's equation for Cr^+ . All energy eigenvalues have been obtained to within the limits of machine accuracy. This means that any further adjustment of the energy value would make $\Delta E/E$ of the order of one part in 400. It was found that the differential analyzer makes errors of this order in the generation of $\ln r$. A great deal of this work was accomplished prior to the period covered by this report. More recently, estimates of the energy eigenvalues have been refined, and runs have been repeated. It was found advisable to repeat the best runs so that machine counter errors might be detected and the validity of the machine solution appraised. In some instances poor repeats were obtained due to improper choice of scales; this is likely to occur when a quantity goes through zero very slowly. The solutions of the six separate Schrödinger equations were all accurately repeated.

The possibility of applying the W.K.B. method to the asymptotic "tails" of the radial wave functions was investigated. If one writes Schrödinger's equation as $d^2y/dr^2 + f(r)y = 0$, the function $f(r)$ changes too rapidly for the use of this method. As a result, the normalization constants have been determined by drawing in a tail, thus forcing the radial wave functions asymptotically to zero. This can be done, in our opinion, without introducing unrealistic errors into the results.

Work was started on the calculation of the new potential field for the 3d electrons in order to attain a higher degree of self-consistency. The following table compares the calculated values of $-Z_0^*(3d, p)$ with the original estimates.

$p = \ln r$	$-Z_0^*$ estimated	$-Z_0^*$ calculated
-3.500	5.000	5.000
-1.350	4.99	4.980
-1.050	4.93	4.927
-0.800	4.825	4.821
-0.600	4.655	4.628
0.000	3.440	3.380
0.150	2.993	2.930
0.450	2.068	2.000
0.650	1.550	1.420
1.100	0.400	0.425
1.350	0.115	0.140
1.600	0.015	0.025

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The work on Cu^+ has been advanced to the point where all six radial wave functions have been determined to within the limits of machine accuracy. All solutions have been repeated successfully. The consistency of this method will be checked.

G. W. Pratt, Jr.

C. ENERGY BANDS IN SOLIDS

The basis of most calculations of energy bands in solids has been the cellular method, developed by Wigner and Seitz, and Slater (1). A crystalline solid is divided into polyhedral cells, one of which is centered about each atom of the crystal. A suitable, spherically symmetrical, one-electron potential is assumed in each cell, and from Schrödinger's equation are obtained the corresponding one-electron wave functions. There now arises the boundary-value problem of maintaining continuity of the wave function and of its derivative in passing from one cell to an adjacent one. By solving this problem, one finds the allowed energy bands in the crystal. Because of mathematical difficulties, boundary conditions are usually satisfied only at a finite number of points on the surface of each cell, so that the resulting wave functions and energy bands are approximate. By applying this method to the case of the empty lattice, i.e. constant potential, Shockley (2) has shown that the approximation is good only in the first Brillouin zone.

Slater (3) has proposed the following alternative method. The polyhedral cells are replaced by spheres surrounding each atom, and a constant potential is assumed in the regions not enclosed by the spheres. Atomic wave functions inside the spheres must now be matched with plane waves outside the spheres. Slater used a perturbation calculation in solving this boundary-value problem and obtained a rather complicated-looking answer, a result which has apparently discouraged people from applying this method to numerical calculation.

Very recently it has been found that the boundary-value problem involved in Slater's method can be solved exactly by elementary methods, and the solution can be cast in a form which is sufficiently simple to insure the practicability of applying it to numerical calculation. The allowed values of energy are obtained by solving the determinantal equation

$$\det G_{ip} = 0$$

where $p = n, l$;

and

$$G_{inl} = j_l \left[R_n \frac{u'_{nl}}{u_{nl}} - k_i R_n \frac{j'_l}{j_l} \right]$$

where R_n is the argument of the radial wave function u_{nl} and $k_i R_n$ is the argument of the spherical Bessel function j_l . Here $\vec{k}_i = \vec{k} + \vec{K}_i$, where \vec{K}_i is the vector separating the centers of the first and the i 'th cells in reciprocal lattice space, and \vec{k} takes on any

value within the first cell. The index l is the azimuthal quantum number of the radial wave equation. The index n ranges over the number of different types of atoms in the crystal. Thus, in a monatomic crystal the index n may be dispensed with. R_n is the radius of the sphere surrounding the n 'th atom. The primes in the above equation denote differentiation. Note that the energy enters this equation only implicitly through the radial wave function u_{nl} .

When Shockley's test (2) of the empty lattice is applied to this equation, the correct free-electron energy dependence, $E = k_i^2$, is obtained by inspection. The equation also immediately gives correct results in the two limiting cases of vanishing wave vector ($k = 0$) and of indefinitely large lattice distance (isolated atoms).

This method is being applied to the calculation of wave functions and energy bands in lithium. The atomic potential used is that of Fock and Petrashen (4). For all but the very lowest values of l , u_{nl} can be very closely approximated by a hydrogen-like wave function. It is hoped that the roots of the determinantal equation will converge rapidly enough to allow the approximation of using only the first few rows and columns of the infinite determinant.

R. H. Parmenter

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D. THEORY OF MOLECULAR OXYGEN

An analysis of the electronic energy states of molecular oxygen has been started. It is felt that the oxygen molecule can serve as a useful model for the more complex configuration of a ferromagnetic solid. The problem has been taken as that of the bonding of the eight electrons originating in the atomic 2p levels. The degeneracies inherent in this problem approach those involved in the bonding of d shell electrons of ferromagnetic materials. What is hoped for is a detailed, quantitative following-through of the various combinations of the many possible configurations; the outcome of all this mixing is, of course, a triplet ground state ($^3\Sigma_g^-$). An understanding of the competition between coulomb energies, exchange energies of electrons belonging to the same ion core, and exchange energies of different ion core electrons will be emphasized, since this seems to be the crux of the ferromagnetic problem.

Both the valence-bond (Heitler-London) and molecular orbital (Bloch-Mulliken) methods will be used. This double attack provides a small-scale model for another

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related problem. As a rule, the two methods are used in clearly defined, mutually exclusive areas of applicability. Ferromagnetism seems to fit into the intermediate region. Using both starting points for a perturbation calculation on oxygen, and then varying the interatomic distance to get into the regions dominated by one or the other, should reveal the quantitative aspects of that intermediate section and the mode of accommodation of the inappropriate technique to the region belonging to the other.

Work has been started on a valence-bond setup. Overlap integrals, "higher" exchange integrals are not being neglected; their actual values are not known as yet.

A. Meckler

E. THEORY OF FERROELECTRICITY

The theory of ferroelectricity of barium titanate, recently treated in Phys. Rev. 78, 748 (1950) by the writer, is being extended by Mr. H. C. Schweinler to other types of crystal structure which are also known experimentally to lead to ferroelectricity.

J. C. Slater

F. QUANTUM THEORY OF ANTIFERROMAGNETISM

This work is described in forthcoming Technical Report No. 172.

L. Tisza, R. J. Harrison

G. SOFT X-RAY VACUUM SPECTROGRAPH

The spectrograph has been focused and calibrated over the normal working range of the proposed experimentation by means of the high-vacuum spark in conjunction with Eastman 35-mm SWR film. Two separate sources were used. For the region from 230 Å to 400 Å we have used NaOH fused into aluminum electrodes, and from 130 Å to 230 Å, powdered Al₂O₃ in similar electrodes. The power supply was modified to supply high instantaneous currents at peak voltage by utilizing a kenotron charging circuit and four 0.05-μf condensers in series. These were discharged across the vacuum electrodes by means of a rotary spark gap. The voltage used was in the range of 50-70 kv. It was not possible to identify the lines above 240 Å definitely; those below this value were established to be the four oxygen lines: 207.8, 215.2, 233.6, and 238.5; and the four aluminum lines: 129.7, 130.4, 160.1 and 161.7. At all points in the calibrated range the resolution is of the order of 0.1 Å or better, indicating a voltage resolution for energy band determinations of approximately 0.02 volt. The calibration was transferred to the photomultiplier by means of a surveyor's transit so that we now have a plot of wavelength versus the multiplier drive shaft rotation. Since it was impossible to use the spark with the multiplier, we plan to correct any small transfer errors by observing the sharp edge of the solid aluminum emission band. The slit-width of the photomultiplier has been adjusted to match the resolution quoted above.

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We are now installing the evaporating system and cleaning and reassembling the X-ray chamber in preparation for the solid-state emission experiments.

G. G. Harvey, E. M. Gyorgy, R. H. Kingston

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H. PARAMAGNETIC RESONANCE EXPERIMENTS

We have greatly extended our measurements on paramagnetic crystals. A number of very interesting phenomena have shown up, some of them quite unexpected. Before discussing our results we mention a few important changes which have been made in the apparatus.

We have modified our electromagnet so that we can reach fields up to about 6700 gauss. This field is necessary for reaching all of the lines in the paramagnetic spectra of the crystals which we are studying. We have gone to the method of continuous sweep of the magnetic field, so that we can display the spectrum of the salt being tested on an oscilloscope, plotting absorption against magnetic field. Such curves are traced directly on paper by means of a simple optical system. A typical traced curve is shown in Fig. III-1. To establish the exact value of the magnetic field for each of the peaks, the

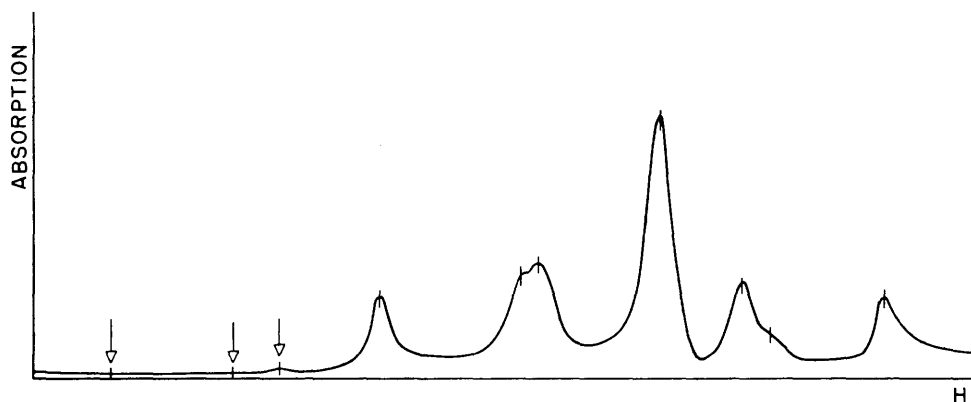


Fig. III-1 Oscilloscope tracing of dilute ammonium chrome alum spectrum. External field \perp (III) plane of crystal. Arrows point to the positions where forbidden lines have been found. $T = 300^\circ\text{K}$.

varying component of the field is slowly decreased while the static value is maintained at the value which keeps a given peak at the center of the oscilloscope trace. Measurements of the static component of the field are made when the a-c field has been reduced to zero.

A special cavity has been made for use when it is necessary to take measurements

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at a number of angles of the crystal with respect to the external magnetic field. The cavity is made to take a small plexiglass rod on which the crystal may be fastened. The rod extends outside the cavity and can be rotated when the cavity is inside the low temperature dewar flasks by means of a control which extends outside the dewars. The angle of the crystal is determined by observations of a mark cut in the end of the rod which is viewed through a simple optical system. Accuracy of $\pm 1^\circ$ in reading the angle is possible.

A number of different kinds of hydrated chrome alum single crystals have been investigated. Two unexpected phenomena had shown up in our measurements of the ammonium chrome alum, and in order to understand them we have run measurements on chrome alums of potassium, rubidium, and cesium. One of these phenomena, which has now been observed in all of the alums tested, was the appearance of a very low intensity peak in the low field region of the spectrum; it had not been accounted for on the basis of simple theory. It turns out that in all cases this line corresponds exactly to one or more forbidden transitions. Further experiments have been made on diluted ammonium and potassium chrome alums, in which about 7 out of every 8 chrome ions have been replaced by aluminum. As has been shown by Whitmer et al (1), dilution affects the Stark splitting produced by the crystalline electric fields and hence modifies the positions of the resonance lines due to this splitting. In this case as well as in the case of the normal salts, the positions of the extra lines correspond to the predicted positions for the forbidden lines. In the case of dilute ammonium chrome alum, as shown in Fig. III-1, we have been able to find three forbidden lines; all of them occur at predicted positions.

The second phenomenon which we have studied has to do with the spectra of ammonium and potassium chrome alum at low temperatures. In both of these salts there is a transition which occurs (sharply in the ammonium and gradually in the potassium alum) as the temperature is lowered. Below the transition temperature the spectrum is very much more complicated. It has been found by another method (2) that there are two Stark splittings below the transition temperature. This is already very surprising, in view of the fact that the spectroscopic state of the paramagnetic chromic ion (${}^4F_{3/2}$) is at most two-fold degenerate in the absence of a magnetic field, and hence can be split into at most two levels (one splitting) by the applied magnetic field. In the case of our experiments we have tentatively assigned three splittings to the ammonium salt and two splittings to the potassium salt in order to explain our results. The values of the splittings we assign for best agreement with the data are in quite good agreement with the values given by Bleaney, except that he did not find the third splitting in the case of ammonium chrome alum.

The situation is in fact still more complicated, since the spectra below the transition temperature no longer have certain symmetry properties which they should have

according to theory. Until this situation is understood, our assignment of splitting values is necessarily very tentative. A theoretical study is being made of this problem by Dr. Julian Eisenstein, and further experimental work is in progress.

In our studies of some rare earth we are collaborating with Prof. F. H. Spedding and Mr. Buell Ayers who have provided the single crystals we are using. We have investigated in greater detail the spectrum of $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ at a number of angles with respect to the external field. Our results can be fairly simply described in terms of at least two ions per unit cell in the crystal, and a large nuclear hyperfine structure. Each ion gives rise to a single line which shows anisotropy in that the position of the peak is a function of the orientation of the crystal with respect to the magnetic field. For a certain direction the two peaks are superposed, and show six hyperfine structure lines, spaced 15 gauss apart. As the angle is changed, the number of hyperfine structure lines in each peak decreases in an orderly fashion, until each peak has become a sharp single peak. In the meantime, the hyperfine lines have spread out over the entire magnetic spectrum, and show up as very small individual peaks spaced as much as 200 gauss apart. We have not yet completed the study of this material, but it is clear that at certain angles the effect of the nucleus is very large. Somewhat similar effects are found in the single crystal of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. These studies are not yet completed.

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