

NUMERICAL METHODS AND AUTOMATIC COMPUTING IN
ATOMIC THEORY

A SYMPOSIUM on the application of automatic computing machines to the problems of extra-nuclear atomic theory was held in the University Mathematical Laboratory, Cambridge, on December 9 last. The subject was introduced by Prof. D. R. Hartree (Cavendish Laboratory, Cambridge), who began by pointing out that problems in this field are usually concerned with the solution of Schrödinger's equation, $H\Psi = E\Psi$, subject to appropriate boundary conditions. For many-electron systems it is necessary to resort to approximation in attempting to obtain solutions of this equation. Two important classes of problem are those of an electron in a bound state and in a free state: the former is characterized by E being negative and assuming a discrete, unknown value corresponding to each bound state; in the latter problem, E is positive and known for the phenomenon being studied, such as elastic or inelastic collision of an electron with an atomic system. Prof. Hartree continued with a more detailed account of the solution of the stationary-state equation for complex atoms along the lines of a previous paper of his (*Rep. Progr. Phys.*, 9; 1946-47). In particular, he outlined the defects of the Slater-Fock approximations in failing to express correlations between the positions of individual electrons in an atomic structure, and possible means of including, in the approximate wave-function adopted, terms expressing these correlations.

This introduction was followed by an account by A. S. Douglas (Mathematical Laboratory, Cambridge) of some recent work on improved approximations to stationary-state solutions using electronic computers. For the class of configurations consisting of a 'core' of closed shells of electrons and a single series electron, the Hartree-Slater-Fock approximation for the wave function of the series electron can be improved by including a polarization potential term in the equations. It is possible to determine by trial an empirical addition to the potential function in such a way as to bring the calculated energies of all terms of the optical spectrum into close agreement with the observed values; the agreement with experiment does not define the additional potential function uniquely. This has been done for Si^{+3} , using the EDSAC to compute the integrals involved in treating the additional potential as a first-order perturbation, and also to solve directly the equation, with exchange, including the additional contribution to the potential. The Runge-Kutta step-by-step method of integration developed by Gill for use on the EDSAC has been adapted for this purpose. An empirical rule for determining the additional potential for other structures has been postulated and is now being tested for Ca^+ .

A second problem investigated by Mr. Douglas concerns the computation of an approximate wave-function for two-electron structures, such as helium, in the ground-state. Schrödinger's equation for helium can be reduced to a partial differential equation in three variables, and this can be solved approximately by solving a related parabolic equation involving an auxiliary independent variable t , the solution of which tends asymptotically to the required

function as t increases. The related equation can be replaced by its finite difference form and solved step by step in t . Exploratory work on the equation for the stationary states of hydrogen by this method indicates that a large number of steps in t may be required, and has disclosed some anomalies in the process of convergence, which are under investigation.

In the afternoon, Dr. R. A. Buckingham (University College, London) gave an account of the use of variational methods of solving two-body and three-body collision problems. For slow electrons the only important contribution to the cross-section for elastic scattering is dependent on the asymptotic phase of the scattered electron. It can be shown that for small, restricted variations of the wave function, this phase is stationary, and this can be used for determining an approximation to the phase by one of the variational methods devised by Hulthén (1944) or Kohn (1948). These methods both involve solution of sets of simultaneous algebraic equations, those of Hulthén's method being quadratic, and those of Kohn's method being linear.

Even comparatively simple approximations to the wave functions for inelastic scattering lead to the necessity for solution of two simultaneous integro-differential equations. Such equations can be solved by the 'distorted wave' method used by Erskine and Massey (1952) in studying the inelastic scattering by hydrogen. Moiseiwitsch (1952) has shown that a variational method of solution is possible, and a finite difference method is at present under investigation. The application of electronic computers to the last two methods is likely to be of special value, in view of the very lengthy computations required. It is interesting that all these procedures have been successfully used in treating collisions between simple nuclei, such as the scattering of neutrons by protons, which have been studied by Swan (1952).

After a short discussion of Dr. Buckingham's paper, Dr. V. E. Price (Department of Theoretical Chemistry, Cambridge) described the use of the EDSAC to compute atomic wave-functions by the variational method due to S. F. Boys (1950-52). The required wave-function is considered expanded as a linear combination of 'serial products' of a complete set of chosen functions, the coefficients of the expansion being determined by use of the variational principle. For stationary-state solutions, the energy-levels are the eigenvalues of a matrix, the elements of which are found by evaluating certain integrals. Each one of these integrals contains not more than four members of the set of functions, and can be evaluated from a recurrence relation, provided a suitable set of functions is chosen. On the EDSAC such an evaluation takes about four seconds. To find the matrix elements from the integrals requires considerable algebraic manipulation, such as matrix multiplication, which can also be done on the machine. The eigenvalues of the resulting matrix, too, can be found by the machine. By taking a sufficiently large matrix, it is possible, in principle, to obtain any required accuracy for the solutions. This is not practicable, however, and it is necessary

to choose the few particular members of the set of functions included in the calculation so that a good approximation is assured. A relatively simple calculation can be made to test the probable importance of omitted terms. Calculations on this principle have been carried out on a number of atoms and ions, including chlorine and sulphur, for which thirteen functions were used.

In the ensuing discussion, Dr. Boys (Cambridge) pointed out that the method used can be extended to find molecular wave-functions, the integral evaluation technique being largely applicable to this problem also. In reply to questions by Prof. Hartree and Dr. O. Bunemann (Cambridge), Dr. Boys said that the method is not likely to be of assistance in the nuclear field at present, since the accurate equations are not known with certainty. In answer to Dr. Buckingham, he said that electron affinities calculated by the method have so far shown disappointing lack of agreement with experiment.

After tea, two short contributions were given by visitors. Mr. W. A. Runciman (General Electric Co., Ltd., Wembley) described a problem connected with the fluorescence of a structure consisting of a potassium chloride lattice, in which some of the potassium ions are replaced by thallium. A first approximation to solution of this problem can be obtained by assuming the thallium ions to be in a free state, and an approximate evaluation of the wave functions by the self-consistent field method has been carried out on the EDSAC.

The final contributor was Dr. R. H. Garstang (University College, London), who mentioned a problem he had met in the analysis of departures from Russell-Saunders coupling; this involved the determination of the diagonal elements of a matrix, given its non-diagonal elements and its characteristic values.

A. S. DOUGLAS

PHYSICAL FACTORS IN RELATION TO BIOLOGICAL ACTIVITY OF INSECTICIDES

A MEETING of the Crop Protection Panel of the Agriculture Group of the Society of Chemical Industry was held in the rooms of the Chemical Society in London on February 16, when papers on "Physical Factors in Relation to Biological Activity of Insecticides" were read. Dr. R. A. E. Galley was in the chair.

Mr. C. T. Lewis (Imperial College of Science and Technology, London) discussed factors affecting the adhesion of dry particles of uniform size to active insects. Experiments with selected dyestuffs have shown that dry lipid-soluble particles adhere more readily to the cuticle of blowflies, and to leaf wax, than do lipid-insoluble particles possessing polar groups. Presumably the presence of polar groups lessens the attraction at the solid-solid interface due to Van der Waals forces. The phenomenon has an appreciable influence on the rate of accumulation of particles by flies exposed to deposits. Parallel experiments with insecticidal dusts have yet to be performed; but significant effects may reasonably be expected since contact insecticides are lipid-soluble and most diluent dusts are calcium or magnesium silicates.

Mr. Lewis also considered the effect of the 'cleaning' reactions of a treated fly on the retention and location of accumulated particles. Particles are picked up from a surface on ventral tarsal spines and chemoreceptors, and transferred in cleaning movements to less exposed parts of the body. The frequent cleaning movements result in a balance between the weights of particles at different locations, the head at all times retaining about 7 per cent of the total, the legs 48 per cent, the wings 13 per cent and the abdomen 28 per cent. The pulvilli are not important sites of accumulation, retaining about 2 per cent, and experiments have shown that they are not preferred sites of entry of DDT.

The rate at which fine particles are discarded by a contaminated fly depends largely on the rate at which the continued cleaning movements deliver particles back to the tarsal spines, from which they are returned to the substrate. The rate of loss is rapid until the quantity retained by the fly falls to 20 $\mu\text{gm.}$, but is very slow below 10 $\mu\text{gm.}$

Dr. A. H. McIntosh (Rothamsted Experimental Station) dealt with the effect of certain conditions of test on the toxicity of a single insecticide, illustrated by reference to experiments in which insects were treated by dipping in aqueous suspensions of DDT. The weight retained depends upon the particle size, being greater for needle-shaped crystals than for colloidal particles. Temperature has a notable effect on toxicity, and the temperature coefficient, usually negative, varies with particle size and with humidity. High humidities accentuate the difference between the temperature coefficients of large and small particles.

The fact that poisons do not always have the same speed of action is an additional complication. The values obtained in relative toxicity tests may vary with the time at which observations of kill are made.

Dr. McIntosh also discussed the relation between the contact toxicity of insecticides and their fat-solubility. The first stage in the entry of a contact insecticide is assumed to be solution in the wax layer, and it is often implied that the higher the lipid-solubility the more effective the poison is likely to be. An opposite conclusion can be deduced from Ferguson's principle of drug action, which indicates that different compounds have equal biological activity if applied at the same percentage saturation in the surrounding medium. Dr. McIntosh suggested that if this idea applied to the wax surrounding an insect, compounds of low fat-solubility should be the more effective. He pointed out, however, that there is no relation between the absolute toxicity of DDT and its analogues and lipid-solubility. The view now held is that some degree of lipid-solubility is necessary but it need not be high.

Experiments still in progress lead Dr. McIntosh to conclude that the difference in speed of action between colloid particles and crystals for a range of compounds of the DDT type may be related to the rate of solution of crystals in oil *in vitro*.

Dr. F. Barlow (Colonial Insecticide Research Unit, Porton) enumerated and discussed some factors of importance in the control of adult mosquitoes by residual spraying of houses. Mosquitoes are stimulated to flight after a short time in contact with insecticidal surfaces, and this fact increases the importance of physical factors affecting the availability of deposits.

The best formulation for deposits on absorbent walls is a wettable powder; the dispersing medium