

VI.—An Approximate Determination of the Atomic Wave Functions of Chromium.

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§ 1. INTRODUCTION.

THIS paper presents the results of some approximate calculations, carried out on the model differential analyser described in another paper, of the atomic field of the Cr atom in two states of ionisation. These results are only preliminary, but should form a useful basis from which to start more accurate calculations.

The contributions to Z , which is defined as the total charge lying inside a radius r for an electron in a given wave function, of the $(1s)^2$ to $(3p)^6$ groups were first estimated by interpolating between the values for Ca and Cu and, as a first approximation, these contributions were regarded as known. Some values for the contributions to Z from the $(3d)^1$ group of Cr^{+5} were then obtained and gave an estimate of the field for Cr^{+2} . A field was then obtained for Cr^{+2} by the method of the self-consistent field, and this in turn provided an estimate for the determination of the results for neutral Cr in the state $(3d)^6$. Finally, still assuming the results for the inner groups $(1s)$ to $(3s)$ to be accurate and unchanged by the addition of successive $(3d)$ electrons, the $(3p)^6$ and $(3d)^6$ groups of neutral Cr were made self-consistent. The contributions to Z for the $(3p)^6$ group were left unchanged from the original interpolated values except in the case of neutral Cr.

The results are only rather rough for two reasons. Firstly, the interpolated values of the contributions for the $(1s)$ to $(3s)$ groups, which were left unchanged throughout the cal-

culations, are presumably not accurate, and must differ to some extent from one state of ionisation to another. Secondly the solutions of the P-equation which are required were carried out on the model differential analyser, and may be in error to an extent of 5 per cent. The original interpolated values for the contributions to Z from $(3p)^6$ for neutral Cr, and the final values, are given in Table II. of § 5, as an indication of the probable inaccuracies in the other interpolations, whilst the order of magnitude of the error in using the model differential analyser was found by determining the approximate atomic wave functions of normal H on the machine, and comparing them with values obtained from the analytical wave function.

It was found, especially in the cases of Cr^{+2} and neutral Cr, that the $(3d)$ group is overstable, and it is rather troublesome to handle on this account. The $(3d)$ wave function is also very sensitive to changes in the estimated field because of the small value of the energy parameter ϵ involved in the wave function.

§ 2. THEORY.

If the wave function ψ for a single electron in a central field of potential v is written as

$$\psi(r, \theta, \phi) = [P(r)/r]S_l(\theta, \phi),$$

the radial wave function $P(r)$ satisfies the equation

$$d^2P/dr^2 + [2v - \epsilon - l(l+1)/r^2]P = 0 \quad (1)$$

in which v , ϵ and r are in atomic units.

The usual P-equation (1) is not particularly suited for use on the differential analyser because the solution is an oscillating function of r whose "wave-length" and "amplitude" are small for small r but rapidly increase as r increases. The modified form,

$$d^2(Pr^{-1})/d\rho^2 + [2Z_p r - \epsilon r^2 - (l + \frac{1}{2})^2]Pr^{-1} = 0 \quad (2)$$

(where $\rho = \log r$, and Z_p/r is the potential v at radius r), already used for some work on Hg with the original differential analyser¹ was used instead.

¹ D. R. Hartree, *Phys. Rev.*, Vol. 48, p. 738, (1934).

The solution of (2) is such that the ratios of the radii of successive nodes are roughly the same, and the maxima of (Pr^{-1}) are of the same order. Equation (2) is also convenient for solution on the model differential analyser because firstly, it can be handled with three integrators and an input table, and secondly, the coefficient of (Pr^{-1}) at small r is of convenient

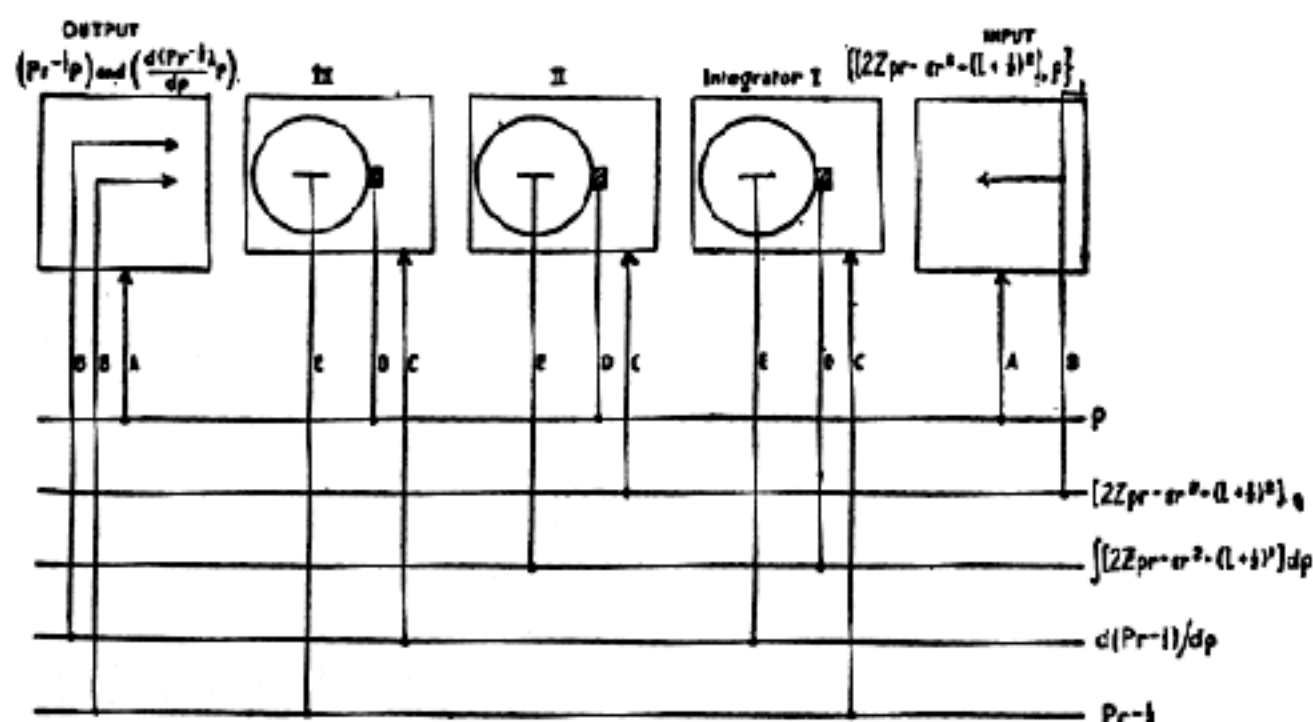


FIG. 1.—Schematic set-up of differential analyser for the solution of the radial wave-equation in the form

$$(d/d\rho)(Pr^{-1}) = - \int [2Z\rho - \epsilon r^2 - (l + \frac{1}{2})^2] Pr^{-1/2} d\rho.$$

where $\rho = \log r$.

Explanation of the Diagram.

- The conventions used in the above are similar to those used by Bush (see previous paper on the model differential analyser). For example,
- The rotation of cross shaft A displaces either an input or an output table.
- The rotation of cross shaft B traverses either a pencil or crosswire across the input or output table.
- The rotation of cross shaft C displaces the integrator carriage.
- The rotation of cross shaft D rotates the integrator disc.
- The rotation of cross shaft E is the rotation of the integrating wheel which rolls on the surface of the integrator disc.

magnitude and does not become infinite. The machine connections are shown on the schematic diagram Fig. 1. This set-up differs from that used by Hartree in the calculations for Hg, since the units of the model machine available were limited to three integrators, an input table, and an output

table. The only difference between the two is that for a given estimated field the method using three integrators requires a different input curve for each trial value of ϵ , whilst in the alternative method a single curve of $2Z_p$ is used for all ϵ , the sum $[-\epsilon r^2 + 2Z_p r]$ is constructed mechanically, and different values of ϵ are obtained by adjusting the displacement of the fourth integrator. A detailed discussion of the modified form of the radial wave equation has been published in connection with the Hg calculations.

§ 3. PROCEDURE.

An outline of the general procedure has been given in § 1. Since Z_p appears explicitly in the radial wave equation, and also in the input plot, it was found convenient to make estimated contributions in terms of Z_p .

The initial displacements of the integrators were determined from a series solution of the P-equation carried out for $r = 0.005$, and from the value of $[2Z_p r - \epsilon r^2 - (l + \frac{1}{2})^2]$ at this radius. If the arbitrary constant involved in the solution is chosen so that the equation can be integrated over the whole range of r without overtravel of the integrators, the initial displacements of integrators II and III must be very small and cannot be made accurately. It was found necessary, especially in the calculations with the $(3d)$ group, to do the solution in different stages, using large values of the arbitrary constant for small r and small values for large r . The setting of the machine at the beginning of each subsequent stage was deduced by noting the readings of the revolution counters driven by the integrator lead screws at the end of the previous stage. Then, by simple division, the displacements corresponding to a smaller value of the arbitrary constant were deduced.

The equation involved in the self-consistent field method which expresses the potential Z_p/r in terms of Z was solved numerically. It was not practicable to do this part of the work on the machine, because totally different set-ups would be required for each stage in the calculations.

The method used for the determination of the characteristic

values of the energy parameter ϵ was one of trial and error; and, although not strictly the best method, it was considered sufficiently accurate for use with the model differential analyser. Solutions of (2) were taken with different estimated values of

TABLE I.

(Pr-1) as a function of $\log r$, for the one-electron wave-functions (unnormalised) for Cr^{+2} ($3d$) and neutral Cr. ($3p$) and ($3d$)

| ρ . | r . | $\text{Cr}^{+2}(3d)$. | $\text{Cr}(3p)$. | $\text{Cr}(3d)$. |
|------------------------|-------|------------------------|-------------------|-------------------|
| - 4.60 | 0.01 | 0.01 | 0.177 | 0.01 |
| - 3.91 | 0.02 | 0.06 | 0.44 | 0.06 |
| - 3.50 | 0.03 | 0.22 | 0.72 | 0.23 |
| - 3.30 | 0.037 | 0.30 | 0.915 | 0.31 |
| - 3.10 | 0.045 | 0.43 | 1.12 | 0.42 |
| - 2.90 | 0.055 | 0.64 | 1.35 | 0.65 |
| - 2.70 | 0.067 | 0.86 | 1.59 | 0.87 |
| - 2.50 | 0.08 | 1.10 | 1.81 | 1.11 |
| - 2.30 | 0.10 | 1.38 | 1.99 | 1.39 |
| - 2.10 | 0.12 | 1.92 | 2.07 | 2.05 |
| - 1.90 | 0.15 | 2.72 | 2.04 | 2.85 |
| - 1.70 | 0.185 | 3.68 | 1.84 | 3.87 |
| - 1.50 | 0.225 | 4.86 | 1.44 | 4.99 |
| - 1.30 | 0.272 | 6.24 | 0.88 | 6.39 |
| - 1.10 | 0.337 | 7.66 | 0.20 | 7.77 |
| - 0.90 | 0.41 | 9.08 | - 0.52 | 9.11 |
| - 0.70 | 0.50 | 10.20 | - 1.17 | 10.13 |
| - 0.50 | 0.61 | 10.90 | - 1.63 | 10.63 |
| - 0.30 | 0.74 | 11.00 | - 1.84 | 10.55 |
| - 0.10 | 0.905 | 10.45 | - 1.77 | 9.79 |
| + 0.10 | 1.105 | 9.40 | - 1.49 | 8.63 |
| 0.30 | 1.35 | 8.00 | - 1.09 | 7.31 |
| 0.50 | 1.65 | 6.48 | - 0.70 | 5.93 |
| 0.70 | 2.01 | 4.88 | - 0.37 | 4.63 |
| 0.90 | 2.46 | 3.50 | - 0.17 | 3.49 |
| 1.10 | 3.00 | 2.24 | - 0.04 | 2.53 |
| 1.30 | 3.67 | 1.28 | | 1.77 |
| 1.50 | 4.48 | 0.60 | | 1.19 |
| 1.70 | 5.46 | 0.10 | | 0.75 |
| 1.90 | 6.69 | 0.01 | | 0.39 |
| 2.10 | 8.17 | | | 0.16 |
| 2.30 | 9.99 | | | 0.04 |
| ϵ | | 1.72 | 2.85 | 0.29 |
| $\int_0^\infty P^2 dr$ | | 165.0 | 2.660 | 166.0 |

ϵ until one was found which best satisfied the condition that $P \rightarrow 0$ as $\rho \rightarrow \infty$. In general this condition was satisfied by interpolating between the results obtained with two slightly different ϵ 's, one greater and the other smaller than the correct value.

§ 4. RESULTS.

Tables I. and II. give the main results as obtained on the model. Table I. gives (Pr^{-1}) as a function of $\log r$ for the one-electron wave functions of the $(3d)$ group of Cr^{+2} and the $(3p)$ and $(3d)$ groups of neutral Cr. The values of ϵ and the normalising factor are given in each case.

Table II. gives the final approximate contributions to Z from the $(1s)^2$ to $(3d)^4$ groups of Cr^{+2} , and from the $(3p)^6$ and $(3d)^6$ groups of neutral Cr. The final contributions to Z from the core electrons $(1s)^2$ to $(3s)^2$ are left unchanged from the originally interpolated values, both in the results for the doubly ionised and for the neutral atom. In both Tables I. and II. r is expressed in atomic units.

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