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# A Self-Consistent Field for Doubly Ionized Chromium*

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A self-consistent field without exchange has been calculated for doubly ionized chromium in the configuration $(3p)^6$ $(3d)^4$. All integrations were carried out numerically with the aid of a calculating machine. The difference between the final and semi-final approximations to $Z_{n,\,l}$ is nowhere greater than ±0.003.

A GLANCE at the periodic table of the elements will show that chromium occurs in the middle of the transition group from scandium to nickel. In the elements of this group the *3d* sub-shells are not full in the sense of the Pauli exclusion principle. Classically considered this feature may be regarded as due to the fact that the attractive force exerted on a *3d* electron by the field of the rest of the atom is not sufficiently large to balance or overcome the centrifugal force due to the orbital angular velocity of the electron—with the result that the electron finds a stable position of dynamic equilibrium in the *4s* shell. It is to be expected that the self-consistent field for chromium will exhibit strongly the kind of "over-stability" in the *3d* sub-shell that was found by Hartree.[1]

The method of the self-consistent field is so well-known that a detailed description is unnecessary here. It is assumed that the ion is described by a simple product function of one-electron functions of the form $[P_{n,\,l}(r)/r]\cdot S(\theta,\,\phi)$. The differential equation satisfied by $P_{n,\,l}$ is

$$\frac{d^2P_{n,\,l}}{dr^2}+\left[\frac{2(Z_p)^{(n,\,l)}}{r}-\epsilon_{n,\,l}-\frac{l(l+1)}{r^2}\right]P_{n,\,l}=0. \quad (1)$$

When the wave functions satisfying the appropriate boundary conditions are known, the field due to a particular sub-group $(n,\,l)$ with $N_{n,\,l}$ electrons is given by $Z_{n,\,l}/r^2$, where

$$Z_{n,\,l}=N_{n,\,l}\int_r^\infty P^2_{n,\,l}dr\Big/\int_0^\infty P^2_{n,\,l}dr. \quad (2)$$

$(Z_p)^{(n,\,l)}$ occurring in (1) is defined by

$$(Z_p)^{(n,\,l)}=C+1+\sum_{n,\,l} Z_{p_{n,\,l}}-\frac{1}{N_{n,\,l}}\cdot Z_{p_{n,\,l}}, \quad (3)$$

where $C$ is the number of electrons removed from the neutral atom to produce the ion. $Z_{p_{n,\,l}}$ is obtained by integrating

$$\frac{dZ_{p_{n,\,l}}}{dr}=\frac{Z_{n,\,l}-Z_{p_{n,\,l}}}{r}. \quad (4)$$

Slater[2] has shown that good approximations to the correct radial wave functions can be obtained by an interpolation method utilizing analytic approximations to wave functions already calculated for other atomic systems. This fact suggests that a crude initial field may be obtained by direct interpolation in the case of Cr III between tabulated values of the contributions to $Z_{n,\,l}$ already determined for $Cl^-$,[1] $K^+$,[3] $Ca^{++}$,[4] $Cu^+$,[1] and $Rb^+$.[5] This interpolation was done graphically. For a given value of the radius, values of $Z_{n,\,l}$ as ordinates were plotted as functions of the atomic numbers of the corresponding atoms. The ordinate of the intersection of the curve drawn through the five points (corresponding to the five ions used for the interpolation) with the ordinate erected at the number corresponding to the atomic number of chromium was taken as the trial value of $Z_{n,\,l}$ for Cr III for that particular value of the radius and sub-shell considered. Subsequent calculations showed that this method is empirically justified for the *K* and *L* shells but is unsatisfactory for the *M*

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[1] D. R. Hartree, Proc. Roy. Soc. **A141**, 281 (1933).

[2] J. C. Slater, Phys. Rev. **32**, 339 (1928).

[3] D. R. Hartree, Proc. Roy. Soc. **143**, 506 (1934).

[4] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A149**, 210 (1935).

[5] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 111 (1927).

shell, primarily because of the double ionization of Cr III in contrast with the lower degree of ionization of the ions compared ($Ca^{++}$ excepted). A table of approximate values of $Z_{n,\,l}$ as calculated by A. Porter[6] was used as a first estimate for the $M$ electrons. (Porter's results are admittedly inaccurate because of the methods he used to determine the energy parameters and the fact that the initial distributions of the core electrons from the $(1s)^2$ to $(2p)^6$ were left unchanged in all subsequent approximations.) In order to integrate (1) it is necessary to choose a trial value of $\epsilon_{n,\,l}$. Very good approximations to the correct energy parameters are furnished by x-ray data in the cases of the $K$ and $L$ electrons. Linear interpolation between the results for $Cu^+$ and $Ca^{++}$ yield values of $\epsilon_{n,\,l}$ satisfactory as first trial values for the $M$ electrons.

Introducing the variable $\eta_{n,\,l}=-P'_{n,\,l}/P_{n,\,l}$, we can write (1) as

$$\eta'_{n,\,l}=\eta^2_{n,\,l}-\epsilon_{n,\,l}-\frac{l(l+1)}{r^2}+\frac{2(Z_p)^{(n,\,l)}}{r}. \quad (5)$$

It is convenient to integrate (5) inwards from $r=\infty$ to the value of the radius at which the last maximum of $P''_{n,\,l}$ counted outwards from $r=0$ occurs. At such a point $\eta_{n,\,l}$ can be compared with $-P'_{n,\,l}/P_{n,\,l}$ obtained from the outward integration of (1). The correct value of $\epsilon_{n,\,l}$ will give a smooth join. When the point of join is selected as above, it turns out that curves for

TABLE I. *Tabulation of the calculated values of* $Z_{n,\,l}$.

| $r$ | $(1s)^2$ | $(2s)^2$ | $(2p)^6$ | $(3s)^2$ | $(3p)^6$ | $(3d)^4$ |
|---|---|---|---|---|---|---|
| 0.000 | 2.000 | 2.000 | 6.000 | 2.000 | 6.000 | 4.000 |
| .005 | 1.996 | 2.000 | 6.000 | 2.000 | 6.000 | 4.000 |
| .010 | 1.975 | 1.998 | 6.000 | 2.000 | 6.000 | 4.000 |
| .015 | 1.929 | 1.994 | 6.000 | 1.999 | 6.000 | 4.000 |
| .020 | 1.859 | 1.988 | 6.000 | 1.998 | 6.000 | 4.000 |
| .025 | 1.767 | 1.981 | 5.999 | 1.997 | 6.000 | 4.000 |
| .030 | 1.660 | 1.973 | 5.997 | 1.996 | 6.000 | 4.000 |
| .035 | 1.540 | 1.964 | 5.995 | 1.995 | 6.000 | 4.000 |
| .040 | 1.415 | 1.956 | 5.991 | 1.994 | 6.000 | 4.000 |
| .045 | 1.288 | 1.948 | 5.984 | 1.993 | 6.000 | 4.000 |
| .050 | 1.165 | 1.941 | 5.976 | 1.992 | 5.997 | 4.000 |
| .06 | .928 | 1.931 | 5.950 | 1.990 | 5.994 | 4.000 |
| .07 | .723 | 1.925 | 5.910 | 1.990 | $5.988^5$ | 4.000 |
| .08 | .552 | 1.923 | 5.852 | $1.989^5$ | 5.981 | 4.000 |
| .09 | .415 | 1.923 | 5.776 | $1.989^5$ | 5.972 | 4.000 |
| .10 | .308 | 1.922 | 5.680 | 1.989 | 5.960 | 4.000 |
| .11 | .225 | 1.919 | 5.564 | 1.989 | 5.947 | 4.000 |
| .12 | .163 | 1.912 | 5.430 | 1.987 | 5.931 | 4.000 |
| .13 | $.117^5$ | 1.898 | 5.277 | 1.985 | 5.914 | 4.000 |
| .14 | .084 | 1.878 | 5.109 | 1.982 | 5.896 | 3.999 |
| .15 | .059 | 1.850 | 4.928 | 1.978 | 5.876 | 3.999 |
| .16 | .042 | 1.815 | 4.735 | $1.972^5$ | 5.857 | 3.998 |
| .18 | .020 | 1.723 | 4.324 | 1.960 | 5.818 | 3.997 |
| .20 | .010 | 1.607 | 3.896 | 1.945 | 5.782 | 3.995 |
| .22 | .005 | 1.473 | 3.467 | 1.929 | 5.750 | 3.992 |
| .24 | .001 | 1.329 | 3.052 | 1.915 | 5.725 | 3.988 |
| .26 | $.000^5$ | 1.182 | 2.658 | 1.902 | 5.707 | 3.982 |
| .28 |  | 1.038 | 2.294 | 1.892 | 5.695 | 3.975 |
| .30 |  | .897 | 1.964 | 1.885 | 5.688 | 3.966 |
| .32 |  | .773 | 1.667 | 1.880 | 5.685 | 3.955 |
| .36 |  | .554 | 1.179 | 1.877 | $5.684^5$ | 3.927 |
| .40 |  | .384 | .814 | 1.877 | $5.677^5$ | 3.889 |
| .44 |  | .262 | .552 | 1.872 | 5.650 | 3.842 |
| .48 |  | .167 | .368 | 1.857 | $5.592^5$ | 3.785 |
| .52 |  | .110 | .241 | 1.827 | 5.498 | 3.719 |
| .56 |  | .072 | .157 | 1.780 | 5.364 | 3.644 |
| .60 |  | .044 | .100 | $1.717^5$ | 5.193 | 3.562 |
| .64 |  | .028 | .064 | 1.640 | 4.988 | 3.473 |
| .68 |  | .017 | .040 | 1.550 | 4.755 | 3.380 |
| .72 |  | .010 | .025 | 1.452 | 4.501 | 3.282 |
| .76 |  | .006 | .016 | $1.347^5$ | 4.231 | 3.181 |
| .80 |  | .004 | .010 | $1.240^5$ | 3.954 | 3.077 |
| .84 |  | .002 | .006 | 1.133 | 3.673 | 2.973 |
| .88 |  | .001 | .004 | 1.028 | 3.394 | 2.867 |
| .92 |  | .001 | .002 | .927 | $3.120^5$ | 2.762 |
| .96 |  | $.000^5$ | .001 | .831 | 2.856 | 2.658 |
| 1.00 |  |  | .001 | .741 | 2.604 | 2.554 |
| 1.04 |  |  | $.000^5$ | .657 | 2.364 | 2.452 |
| 1.08 |  |  |  | $.580^5$ | 2.139 | 2.352 |
| 1.12 |  |  |  | $.510^5$ | 1.929 | 2.254 |
| 1.16 |  |  |  | .447 | 1.734 | 2.158 |
| 1.20 |  |  |  | .390 | 1.554 | 2.065 |
| 1.24 |  |  |  | $.339^5$ | 1.391 | 1.974 |
| 1.28 |  |  |  | .294 | 1.234 | 1.886 |
| 1.32 |  |  |  | .256 | 1.115 | 1.801 |
| 1.36 |  |  |  | .221 | .993 | 1.718 |
| 1.40 |  |  |  | .191 | .882 | 1.639 |
| 1.44 |  |  |  | .164 | .782 | 1.561 |
| 1.5 |  |  |  | .130 | .652 | 1.453 |
| 1.6 |  |  |  | .088 | .478 | 1.283 |
| 1.7 |  |  |  | .059 | $.348^5$ | 1.130 |
| 1.8 |  |  |  | .040 | .251 | .992 |
| 1.9 |  |  |  | .027 | .179 | .869 |
| 2.0 |  |  |  | .018 | .128 | .760 |
| 2.1 |  |  |  | .011 | .091 | .663 |
| 2.2 |  |  |  | .008 | .064 | .577 |
| 2.3 |  |  |  | .005 | $.045^5$ | .501 |
| 2.4 |  |  |  | .003 | .032 | .423 |
| 2.6 |  |  |  | .001 | .016 | .322 |
| 2.8 |  |  |  |  | .008 | .229 |
| 3.0 |  |  |  |  | .004 | .175 |
| 3.2 |  |  |  |  | .002 | .123 |
| 3.4 |  |  |  |  |  | .085 |
| 3.6 |  |  |  |  |  | .060 |
| 3.8 |  |  |  |  |  | .042 |
| 4.0 |  |  |  |  |  | .030 |
| 4.4 |  |  |  |  |  | .015 |
| 4.8 |  |  |  |  |  | .007 |
| 5.2 |  |  |  |  |  | .004 |
| 5.6 |  |  |  |  |  | .002 |
| 6.0 |  |  |  |  |  | .001 |

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[6] A. Porter, Mem. Manchester Phil. Soc. **79** (1935).

which values of $\eta_{n,\,l}$ and $-P'_{n,\,l}/P_{n,\,l}$ at the point of join are plotted as functions of $\epsilon_{n,\,l}$ closely approximate straight lines over a surprisingly large range of values of $\epsilon_{n,\,l}$ as long as $Z_{n,\,l}$ is left unchanged. The solution of (1) is completed by integrating

$$\log_\epsilon P_{n,\,l}\Big]_{r_1}^{\infty} = -\int_{r_1}^{\infty} \eta_{n,\,l}\,dr, \qquad (6)$$

where $r_1$ is the value of the radius at which the join is made.

In integrating (4) and in normalizing $P_{n,\,l}$, a method of mechanical quadrature based upon the interpolation formulae of Stirling and Bessel and perfected by Milne[7] proved to be quite satisfactory. Eq. (5) is best solved by the Runge-Kutta method,[7] which has an inherent error smaller than that characteristic of Milne's method. A modification of Milne's method for first-order equations can be applied to second-order equations in which the first derivative is absent.[8] The formulae used in both the Milne method and the Runge-Kutta method involved ordinates instead of differences. If at most only two figures are involved in taking differences, it is perhaps advisable to use difference methods, as has been done by Hartree. Even though the calculations at each step in going from one interval to the next in the ordinate methods are more complicated than in the difference methods, whenever a calculating machine is available, it seems strongly advisable to use ordinates. A larger number of significant figures can usually be carried throughout the entire integration using ordinates instead of differences.

Tabulated values of $Z_{n,\,l}$ were used as bases for further approximations. A strict iterative process does not in every case lead to the fastest rate of convergence to self-consistency; and, indeed, in the case of the $3d$ electrons such a process actually led to a divergence from a self-consistent distribution. In the present calculations the following facts were empirically determined. It was found that the actually calculated values of $Z_{n,\,l}$ offered the best estimates for a new approximation for the $(1s)$,

TABLE II. *Values of the unnormalized wave functions $P_{n,\,l}$. Values of the normalization constants appear at the bottom of the table.*

| $r$ | $(1s)^2$ | $(2s)^2$ | $(2p)^6$ | $(3s)^2$ | $(3p)^6$ | $(3d)^4$ |
|---|---|---|---|---|---|---|
| 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| .005 | .443 | .442$^5$ | .023$^5$ | | | |
| .010 | .786 | .781 | .089 | .781 | .049 | .001 |
| .015 | 1.046 | 1.031 | .188 | 1.030 | .188 | .003 |
| .020 | 1.237$^5$ | 1.204 | .316 | 1.201 | .315 | .007 |
| .025 | 1.373 | 1.312 | .465 | 1.306 | .465 | .013 |
| .030 | 1.463 | 1.364 | .633 | 1.354$^5$ | .631 | .021 |
| .035 | 1.516 | 1.370 | .813$^5$ | 1.355 | .810 | .033 |
| .040 | 1.539 | 1.336 | 1.004 | 1.316 | .999 | .047 |
| .045 | 1.538 | 1.269 | 1.201 | 1.243 | 1.193 | .065 |
| .050 | 1.518 | 1.175 | 1.402 | 1.142 | 1.390 | .086 |
| .06 | 1.439 | .925 | 1.806 | .877 | 1.783 | .138 |
| .07 | 1.327 | .620 | 2.203 | .556 | 2.162 | .204 |
| .08 | 1.199 | .284 | 2.580 | .205 | 2.515 | .285 |
| .09 | 1.067 | −0.064 | 2.931 | −0.155 | 2.835 | .379 |
| .10 | .938 | −0.410 | 3.250 | −0.509 | 3.115$^5$ | .487 |
| .11 | .817 | −0.745 | 3.536 | −0.847 | 3.353 | .607 |
| .12 | .706 | −1.060 | 3.787 | −1.160 | 3.552 | .739 |
| .13 | .606 | −1.352 | 4.002 | −1.443 | 3.702 | .882 |
| .14 | .517 | −1.617 | 4.183 | −1.692 | 3.807 | 1.036 |
| .15 | .439 | −1.854 | 4.330 | −1.905 | 3.870 | 1.198 |
| .16 | .372 | −2.063 | 4.446 | −2.081 | 3.891 | 1.369 |
| .18 | .263 | −2.396 | 4.501 | −2.325 | 3.821 | 1.733 |
| .20 | .184 | −2.626 | 4.637 | −2.432 | 3.617 | 2.119 |
| .22 | .127 | −2.765 | 4.600 | −2.417 | 3.300 | 2.522$^5$ |
| .24 | .086 | −2.828 | 4.501 | −2.297 | 2.892 | 2.937 |
| .26 | .057 | −2.829 | 4.351 | −2.090 | 2.412 | 3.357 |
| .28 | .036 | −2.780 | 4.165 | −1.813 | 1.878 | 3.778 |
| .30 | .020 | −2.693$^5$ | 3.954 | −1.483 | 1.306 | 4.197 |
| .32 | .007$^5$ | −2.579$^5$ | 3.726 | −1.113 | .711 | 4.609$^5$ |
| .36 | .000 | −2.300$^5$ | 3.251 | −0.306 | −0.506 | 5.403 |
| .40 | | −1.993 | 2.781 | 0.528 | −1.697 | 6.141 |
| .44 | | −1.689 | 2.343 | 1.329 | −2.810 | 6.809 |
| .48 | | −1.407 | 1.949 | 2.061 | −3.811 | 7.402 |
| .52 | | −1.155 | 1.604 | 2.701 | −4.684 | 7.915 |
| .56 | | −0.938 | 1.309 | 3.240 | −5.421 | 8.351 |
| .60 | | −0.755 | 1.060$^5$ | 3.675 | −6.024 | 8.713$^5$ |
| .64 | | −0.600 | 0.854 | 4.011 | −6.498$^5$ | 9.007 |
| .68 | | −0.478 | .684 | 4.255 | −6.855 | 9.237 |
| .72 | | −0.377 | .545 | 4.417 | −7.105 | 9.411 |
| .76 | | −0.296 | .433 | 4.507$^5$ | −7.262 | 9.536 |
| .80 | | −0.231 | .343 | 4.536 | −7.337 | 9.617 |
| .84 | | −0.180 | .270 | 4.514 | −7.342 | 9.660 |
| .88 | | −0.139 | .213 | 4.449 | −7.290 | 9.671 |
| .92 | | −0.108 | .167 | 4.350 | −7.189 | 9.654 |
| .96 | | −0.084 | .131 | 4.225 | −7.049 | 9.613 |
| 1.00 | | −0.064 | .103 | 4.079 | −6.877 | 9.553 |
| 1.04 | | −0.050 | .080 | 3.919 | −6.681 | 9.475 |
| 1.08 | | −0.038 | .063 | 3.748 | −6.466 | 9.383 |
| 1.12 | | −0.029 | .049 | 3.571 | −6.237 | 9.279$^5$ |
| 1.16 | | | .038 | 3.391 | −5.999 | 9.166 |
| 1.20 | | | | 3.211 | −5.755 | 9.044 |
| 1.24 | | | | 3.029 | −5.481 | 8.915 |
| 1.28 | | | | 2.852 | −5.228 | 8.780 |
| 1.32 | | | | 2.680 | −4.981 | 8.641 |
| 1.36 | | | | 2.513 | −4.740 | 8.498 |
| 1.40 | | | | 2.352 | −4.512 | 8.351$^5$ |
| 1.44 | | | | 2.198 | −4.264 | 8.203 |
| 1.50 | | | | 1.970 | −3.871$^5$ | 7.977 |
| 1.60 | | | | 1.645 | −3.414$^5$ | 7.594 |
| 1.70 | | | | 1.363$^5$ | −2.922 | 7.210 |
| 1.90 | | | | .922 | −2.156 | 6.451 |
| 2.0 | | | | .733 | −1.789 | 6.081$^5$ |
| 2.1 | | | | .613 | −1.563 | 5.722 |
| 2.2 | | | | .497 | −1.321 | 5.373 |
| 2.3 | | | | .403 | −1.117$^5$ | 5.036 |
| 2.4 | | | | .325 | −0.943 | 4.744 |
| 2.6 | | | | .210 | −0.656 | 4.105 |
| 2.8 | | | | .135 | −0.442 | 3.554 |
| 3.0 | | | | .108 | −0.309 | 3.059 |
| 3.2 | | | | .084 | −0.258 | 2.625 |
| 3.4 | | | | | −0.214 | 2.232 |
| 3.6 | | | | | −0.178 | 1.897 |
| 3.8 | | | | | −0.148 | 1.600 |
| 4.0 | | | | | −0.122 | 1.340 |
| 4.4 | | | | | −0.083 | .932$^5$ |
| 4.8 | | | | | | .645 |
| 5.2 | | | | | | .441 |
| 5.6 | | | | | | .299 |
| 6.0 | | | | | | .201 |
| $\int_0^\infty P^2_{n,\,l}\,dr$ | 0.1871 | 2.1877 | 5.9898 | 15.3101 | 46.095 | 142.115 |

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[7] J. B. Scarborough, *Numerical Mathematical Analysis* (Johns Hopkins Press, Baltimore, 1930).

[8] Bull. Nat. Research Council, No. 92 (1935).

(2*s*), and (2*p*) groups. For the (3*s*) and (3*p*) groups best rates of convergence were obtained by adding to the results of the preceding approximation two-thirds of the difference between the results of the preceding and immediate approximations to obtain an estimated table for the immediately following calculations. In the case of the (3*d*) electrons, only one-half the difference between successive approximations was added in the above manner to obtain the best results.

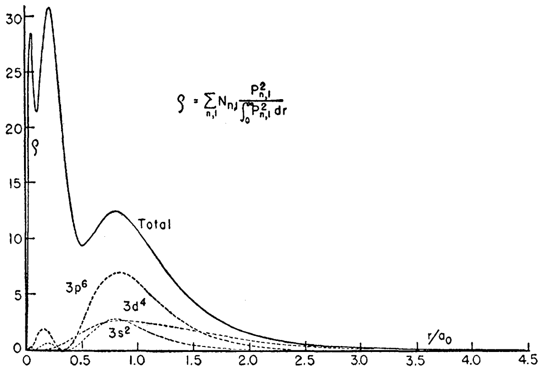

FIG. 1. Radial charge distributions for individual sub-shells and total charge distribution.

In all, three approximations were made for the (1*s*), (2*s*) and (2*p*) sub-groups, and seven for the outer electrons; the distributions of the inner groups were left unchanged from the results of the third approximation for those sub-shells.

## RESULTS

Table I gives a complete tabulation of the finally calculated values of $Z_{n,\,l}$. Nowhere does the difference between the calculated results and the results of the immediately preceding approximation differ by more than ±0.003. A tabulation of the unnormalized wave functions, $P_{n,\,l}$, is given in Table II with the normalization constants given below the table. $P_{n,\,l}$ was calculated throughout to at least five significant figures, and it is probable that the values of $P_{n,\,l}$ are everywhere correct to at least two units in the third decimal place. The energy parameters (in atomic units) which characterize the self-consistent field are given in Table III. The radial charge distributions for the individual sub-shells (from (3*s*) to (3*d*)) are plotted along with the total radial charge distribution (the full-line curve) in Fig. 1. A greater accuracy than is customary in self-consistent field calculations has been aimed at here, since, as has been pointed out by Hartree[9] the exchange corrections can be rather accurately estimated from accurate solutions of the self-consistent field without exchange with the aid of Fock's equations.

TABLE III. *Energy parameters in atomic units which characterize the self-consistent field.*

| | | | | | | |
|---|---|---|---|---|---|---|
| $\epsilon_{n,\,l}$ | 442.11 | 50.845 | 44.242 | 6.972 | $4.946^5$ | 1.797 |
| x-ray | 441.1 | | 42.6 | | | |

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[9] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A157**, 490 (1936).