THE SELF-CONSISTENT FIELD FOR Mo^+

By E. CICELY RIDLEY

Communicated by D. R. Hartree

Received 31 January 1955

ABSTRACT. The results of a self-consistent field calculation without exchange for Mo^+ are presented.

1. *Introduction.* A method of obtaining approximations to the contributions to $Z(r)$ from the electrons in the various wave functions of an atom has been described in the previous paper (5). It was desirable to test this method by using such approximations as first estimates in the calculation of a self-consistent field without exchange. Mo^+ was chosen as the structure to be solved. It lies half-way between Rb^+ and Ag^+, both of which are known structures, and the separation of five units of atomic number in each case is sufficient to make the test a stringent one. Further, a knowledge of the structure of Mo^+ should make it possible to interpolate accurately for other atoms in the second long period.

2. *The method of calculation.* Estimates of the contributions to $Z(r)$ were obtained by the method explained in (5). For the $(1s)$ to $(4p)$ wave functions, the approximations were derived from the known contributions for Rb^+ (Hartree (4)). For the $(4d)$ contribution, the less reliable results for Ag^+ were used (Black (1)), since Rb^+ has no $(4d)$ electrons.

The calculations were carried out on the EDSAC, the automatic calculating machine at the University Mathematical Laboratory, Cambridge. Basically the methods used were those described by Hartree (3). A few modifications made the computations more suitable for an electronic machine.

The calculation involves the solution of the equations

$$\{d^2/dr^2 + (2/r)[1 + i + \Sigma_{n'l'} q(n'l')\, Z_p(n'l'; r) - Z_p(nl; r)] - \epsilon(nl) - l(l+1)/r^2\}\, P(nl; r) = 0, \tag{1}$$

where i = degree of ionization, $q(n'l')$ = number of electrons having quantum numbers $(n'l')$, $\epsilon(nl)$ is an eigenvalue closely related to the energy of an electron in the (nl) wave function,

$$dZ_p(n'l'; r)/dr = [Z_p(n'l'; r) - Z(n'l'; r)]/r \tag{2}$$

and

$$Z(n'l'; r) = 1 - \int_0^r P^2(n'l'; r_1)\, dr_1. \tag{3}$$

A Runge Kutta integration routine from the EDSAC library of subroutines was used for the integrations (Gill (2)). This performs a step-by-step integration of a set of first-order differential equations. The second-order equation (1) was broken down into

https://doi.org/10.1017/S0305004100030772 Published online by Cambridge University Press

two first-order equations, so that for the wave function (nl) the following set of equations was solved:

$$dP(nl;\, r)/dr = Q(nl;\, r), \tag{4}$$

$$dQ(nl;\, r)/dr = -\{(2/r)\,[1+i+\Sigma' Z_p(n'l';\, r)] - \epsilon(nl) - l(l+1)/r^2\}\, P(nl;\, r), \tag{5}$$

$$dZ(nl;\, r)/dr = -P^2(nl;\, r), \tag{6}$$

$$d\Sigma' Z_p(n'l';\, r)/dr = [\Sigma' Z_p(n'l';\, r) - \Sigma' Z(n'l';\, r)]/r, \tag{7}$$

where $$\Sigma' Z_p(n'l';\, r) = \Sigma_{n'l'} q(n'l')\, Z_p(n'l';\, r) - Z_p(nl;\, r),$$

and similarly for $\Sigma' Z$. The estimated $\Sigma' Z(n'l';\, r)$ is substituted in (7), and the new value of the contribution to $Z(r)$ calculated from (6) after normalization.

$\epsilon(nl)$ was found by successive approximation using a first-order correction suggested by a discussion with A. S. Douglas. When the estimates of the contributions to $Z(r)$ have been substituted, (1) becomes homogeneous and may be written

$$d^2P/dr^2 + (V-\epsilon)\, P = 0, \tag{8}$$

where $V = V(r)$ is the effective potential.

Varying ϵ and P, we find that to the first order

$$\delta\epsilon \int_a^b P^2 dr = [P^2\, \delta(Q/P)]_a^b. \tag{9}$$

Thus, if the equations (4)–(7) are integrated outwards from the origin to r_0 and inwards from large r to r_0 with an estimated eigenvalue, $\epsilon + \Delta\epsilon$, then to the first order,

$$\Delta\epsilon = \left\{ \frac{(Q_x/P_x) - (Q_y/P_y)}{\left(\int_0^r P_x^2 dr_1\right)\Big/ P_x^2 + \left(\int_r^\infty P_y^2 dr_1\right)\Big/ P_y^2} \right\}_{r=r_0}, \tag{10}$$

where the variables for the outward integration bear the suffix x and the suffix y denotes inward integration. This enables a better value of ϵ to be calculated, and the integration is repeated until ϵ is obtained with sufficient accuracy. It is necessary to start with an estimate of ϵ accurate to about 10 %; otherwise the process may converge to yield a wave function with the wrong number of nodes. The program had facilities for adjusting ϵ by trial and error until the process of successive approximation could be used. It is interesting to compare this method of obtaining the eigenvalue with that used by Hartree. The repeated integrations necessary here may be rapidly performed on an automatic machine, but would involve prohibitive hand calculation. Five iterations at most gave ϵ with sufficient accuracy. As the self-consistent field was approached more and more closely, the number of iterations necessary diminished.

Initially, the estimates for the inner electrons were assumed correct and the outer electrons were made self-consistent. Only in the later stages were integrations performed for the inner electrons too. To make the self-consistent process converge for the $(4d)$ wave function it was necessary to take the mean of the estimated and calculated contributions to $Z(r)$ as the estimate for the next stage. It was found that the convergence for $(4p)$, $(4s)$ and $(3d)$ was improved if this procedure was adopted. For other

https://doi.org/10.1017/S0305004100030772 Published online by Cambridge University Press

Table 1. Mo^+ *radial wave functions. Table of P*

r	(1s)	(2s)	(2p)	(3s)	(3p)	(3d)	(4s)	(4p)	(4d)
0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·002	1·500	1·000	0·010	0·300	0·010	0·000	0·100	0·010	0·000
0·004	2·759	1·834	0·038	0·550	0·038	0·000	0·183	0·038	0·000
0·006	3·805	2·519	0·083	0·755	0·083	0·001	0·252	0·083	0·000
0·008	4·666	3·069	0·141	0·919	0·141	0·003	0·306	0·141	0·001
0·010	5·364	3·498	0·212	1·046	0·211	0·005	0·349	0·211	0·002
0·015	6·528	4·117	0·429	1·226	0·428	0·017	0·408	0·428	0·007
0·020	7·065	4·218	0·689	1·247	0·685	0·038	0·415	0·684	0·015
0·025	7·170	3·937	0·973	1·150	0·963	0·070	0·382	0·962	0·028
0·030	6·988	3·380	1·267	0·968	1·248	0·113	0·320	1·246	0·045
0·035	6·624	2·633	1·560	0·728	1·528	0·167	0·239	1·523	0·067
0·040	6·152	1·763	1·845	0·451	1·793	0·234	0·146	1·786	0·094
0·05	5·082	−0·144	2·365	−0·148	2·257	0·404	−0·055	2·242	0·161
0·06	4·034	−2·045	2·799	−0·731	2·606	0·616	−0·250	2·579	0·245
0·07	3·116	−3·772	3·136	−1·240	2·827	0·865	−0·419	2·785	0·344
0·08	2·360	−5·239	3·377	−1·645	2·921	1·145	−0·551	2·859	0·455
0·09	1·760	−6·415	3·529	−1·932	2·895	1·449	−0·643	2·811	0·575
0·10	1·298	−7·301	3·603	−2·102	2·762	1·768	−0·694	2·652	0·700
0·12	0·688	−8·297	3·561	−2·122	2·236	2·432	−0·686	2·071	0·957
0·14	0·356	−8·475	3·342	−1·800	1·467	3·093	−0·561	1·247	1·209
0·16	0·181	−8·103	3·023	−1·247	0·565	3·717	−0·357	0·299	1·441
0·18	0·091	−7·406	2·659	−0·564	−0·381	4·282	−0·113	−0·676	1·642
0·20	0·045	−6·551	2·290	0·168	−1·306	4·773	0·143	−1·605	1·808
0·225	0·019	−5·432	1·855	1·065	−2·362	5·273	0·445	−2·626	1·959
0·25	0·008	−4·376	1·472	1·870	−3·264	5·644	0·702	−3·439	2·047
0·275	0·003	−3·451	1·150	2·546	−3·989	5·895	0·899	−4·020	2·076
0·30	0·001	−2·675	0·887	3·076	−4·536	6·038	1·030	−4·368	2·050
0·35	—	−1·548	0·512	3·719	−5·153	6·056	1·104	−4·433	1·861
0·40	—	−0·865	0·287	3·907	−5·271	5·817	0·970	−3·826	1·531
0·45	—	−0·471	0·158	3·782	−5·054	5·419	0·696	−2·766	1·109
0·50	—	−0·252	0·086	3·473	−4·640	4·937	0·340	−1·442	0·631
0·55	—	−0·133	0·046	3·072	−4·130	4·421	−0·049	−0·004	0·126
0·60	—	−0·070	0·024	2·644	−3·592	3·905	−0·434	1·437	−0·384
0·65	—	−0·036	0·013	2·228	−3·067	3·411	−0·793	2·803	−0·882
0·70	—	−0·019	0·007	1·846	−2·581	2·952	−1·111	4·045	−1·357
0·8	—	−0·005	0·002	1·220	−1·767	2·161	−1·596	6·055	−2·211
0·9	—	−0·001	0·001	0·776	−1·170	1·546	−1·882	7·398	−2·913
1·0	—	—	—	0·481	−0·756	1·087	−1·998	8·139	−3·461
1·1	—	—	—	0·292	−0·480	0·754	−1·988	8·398	−3·870
1·2	—	—	—	0·175	−0·301	0·519	−1·893	8·301	−4·162
1·3	—	—	—	0·103	−0·187	0·354	−1·747	7·959	−4·357
1·4	—	—	—	0·061	−0·115	0·240	−1·575	7·464	−4·474
1·6	—	—	—	0·021	−0·043	0·109	−1·221	6·264	−4·540
1·8	—	—	—	0·007	−0·016	0·049	−0·905	5·040	−4·454
2·0	—	—	—	0·002	−0·006	0·022	−0·652	3·946	−4·279
2·2	—	—	—	0·001	−0·002	0·010	−0·460	3·031	−4·052
2·4	—	—	—	—	−0·001	0·004	−0·320	2·297	−3·796
2·6	—	—	—	—	—	0·002	−0·220	1·722	−3·528
2·8	—	—	—	—	—	0·001	−0·150	1·281	−3·258
3·0	—	—	—	—	—	—	−0·102	0·947	−2·992
3·2	—	—	—	—	—	—	−0·069	0·696	−2·736
3·4	—	—	—	—	—	—	−0·046	0·510	−2·491
3·6	—	—	—	—	—	—	−0·031	0·372	−2·261
3·8	—	—	—	—	—	—	−0·021	0·270	−2·045
4·0	—	—	—	—	—	—	−0·014	0·196	−1·844
4·5	—	—	—	—	—	—	−0·005	0·087	−1·408
5·0	—	—	—	—	—	—	−0·002	0·038	−1·060
5·5	—	—	—	—	—	—	−0·001	0·017	−0·788
6·0	—	—	—	—	—	—	—	0·007	−0·580
6·5	—	—	—	—	—	—	—	0·003	−0·422
7·0	—	—	—	—	—	—	—	0·001	−0·305
8·0	—	—	—	—	—	—	—	—	−0·156
9·0	—	—	—	—	—	—	—	—	−0·078
10·0	—	—	—	—	—	—	—	—	−0·038
11·0	—	—	—	—	—	—	—	—	−0·018
12·0	—	—	—	—	—	—	—	—	−0·009
13·0	—	—	—	—	—	—	—	—	−0·004
14·0	—	—	—	—	—	—	—	—	−0·002
15·0	—	—	—	—	—	—	—	—	−0·001

https://doi.org/10.1017/S0305004100030772 Published online by Cambridge University Press

Table 2. Mo^+ *contributions to* Z, *and total* Z_p

r	$(1s)^2$	$(2s)^2$	$(2p)^6$	$(3s)^2$	$(3d)^6$	$(3d)^{10}$	$(4s)^2$	$(4p)^6$	$(4d)^5$	Total Z_p
0·000	2·000	2·000	6·000	2·000	6·000	10·000	2·000	6·000	5·000	42·000
0·002	1·999	2·000	6·000	2·000	6·000	10·000	2·000	6·000	5·000	41·554
0·004	1·990	1·999	6·000	2·000	6·000	10·000	2·000	6·000	5·000	41·113
0·006	1·971	1·997	6·000	2·000	6·000	10·000	2·000	6·000	5·000	40·679
0·008	1·940	1·994	6·000	1·999	6·000	10·000	2·000	6·000	5·000	40·254
0·010	1·896	1·990	6·000	1·998	6·000	10·000	2·000	6·000	5·000	39·840
0·015	1·738	1·975	5·998	1·996	6·000	10·000	1·999	6·000	5·000	38·854
0·020	1·535	1·958	5·993	1·993	5·999	10·000	1·999	6·000	5·000	37·937
0·025	1·312	1·942	5·982	1·990	5·997	10·000	1·998	6·000	5·000	37·081
0·030	1·093	1·928	5·961	1·988	5·993	10·000	1·998	5·999	5·000	36·278
0·035	0·891	1·919	5·929	1·987	5·988	10·000	1·998	5·998	5·000	35·518
0·040	0·713	1·915	5·882	1·986	5·980	10·000	1·998	5·997	5·000	34·792
0·05	0·437	1·913	5·737	1·986	5·956	9·999	1·998	5·994	5·000	33·426
0·06	0·256	1·910	5·520	1·985	5·921	9·997	1·997	5·989	5·000	32·149
0·07	0·145	1·893	5·234	1·981	5·878	9·994	1·997	5·982	5·000	30·948
0·08	0·080	1·852	4·890	1·973	5·830	9·987	1·995	5·976	5·000	29·817
0·09	0·043	1·785	4·503	1·961	5·781	9·976	1·993	5·969	4·999	28·755
0·10	0·023	1·693	4·091	1·946	5·734	9·959	1·991	5·962	4·999	27·759
0·12	0·006	1·450	3·255	1·912	5·660	9·902	1·985	5·953	4·997	25·951
0·14	0·002	1·172	2·480	1·882	5·619	9·802	1·980	5·948	4·995	24·355
0·16	0·000	0·902	1·824	1·864	5·607	9·650	1·978	5·947	4·991	22·930
0·18	—	0·666	1·301	1·858	5·606	9·442	1·977	5·946	4·985	21·636
0·20	—	0·475	0·905	1·857	5·597	9·174	1·977	5·944	4·978	20·445
0·225	—	0·300	0·558	1·853	5·546	8·762	1·976	5·934	4·968	19·073
0·25	—	0·183	0·335	1·832	5·429	8·276	1·971	5·914	4·957	17·813
0·275	—	0·108	0·197	1·786	5·237	7·733	1·961	5·885	4·945	16·655
0·30	—	0·063	0·114	1·711	4·973	7·153	1·948	5·847	4·933	15·594
0·35	—	0·020	0·036	1·490	4·280	5·955	1·913	5·762	4·911	13·756
0·40	—	0·006	0·011	1·214	3·484	4·803	1·881	5·688	4·894	12·261
0·45	—	0·002	0·003	0·935	2·707	3·773	1·861	5·641	4·884	11·054
0·50	—	0·000	0·001	0·688	2·024	2·900	1·852	5·622	4·880	10·072
0·55	—	—	0·000	0·488	1·467	2·187	1·851	5·619	4·879	9·257
0·60	—	—	—	0·335	1·035	1·624	1·849	5·616	4·879	8·562
0·65	—	—	—	0·224	0·715	1·189	1·838	5·596	4·876	7·952
0·70	—	—	—	0·147	0·484	0·860	1·811	5·545	4·869	7·404
0·8	—	—	—	0·060	0·212	0·437	1·701	5·321	4·832	6·441
0·9	—	—	—	0·023	0·089	0·215	1·522	4·930	4·756	5·613
1·0	—	—	—	0·009	0·036	0·103	1·301	4·412	4·640	4·899
1·1	—	—	—	0·003	0·014	0·049	1·069	3·828	4·487	4·289
1·2	—	—	—	0·001	0·005	0·023	0·850	3·233	4·304	3·775
1·3	—	—	—	0·000	0·002	0·010	0·657	2·671	4·098	3·345
1·4	—	—	—	—	0·001	0·005	0·497	2·165	3·877	2·987
1·6	—	—	—	—	0·000	0·001	0·269	1·361	3·414	2·443
1·8	—	—	—	—	—	0·000	0·139	0·819	2·955	2·064
2·0	—	—	—	—	—	—	0·069	0·477	2·522	1·795
2·2	—	—	—	—	—	—	0·033	0·271	2·129	1·600
2·4	—	—	—	—	—	—	0·016	0·151	1·781	1·456
2·6	—	—	—	—	—	—	0·007	0·083	1·477	1·347
2·8	—	—	—	—	—	—	0·003	0·045	1·217	1·265
3·0	—	—	—	—	—	—	0·002	0·024	0·996	1·203
3·2	—	—	—	—	—	—	0·001	0·013	0·810	1·155
3·4	—	—	—	—	—	—	0·000	0·007	0·656	1·118
3·6	—	—	—	—	—	—	—	0·004	0·528	1·090
3·8	—	—	—	—	—	—	—	0·002	0·423	1·068
4·0	—	—	—	—	—	—	—	0·001	0·338	1·052
4·5	—	—	—	—	—	—	—	0·000	0·189	1·026
5·0	—	—	—	—	—	—	—	—	0·104	1·013
5·5	—	—	—	—	—	—	—	—	0·056	1·006
6·0	—	—	—	—	—	—	—	—	0·029	1·003
6·5	—	—	—	—	—	—	—	—	0·015	1·001
7·0	—	—	—	—	—	—	—	—	0·008	1·001
8·0	—	—	—	—	—	—	—	—	0·002	1·000
9·0	—	—	—	—	—	—	—	—	0·000	1·000
10·0	—	—	—	—	—	—	—	—	—	1·000
11·0	—	—	—	—	—	—	—	—	—	1·000

	$(1s)$	$(2s)$	$(2p)$	$(3s)$	$(3p)$	$(3d)$	$(4s)$	$(4p)$	$(4d)$
$\int_0^\infty P^2 dr$	2·2980	10·254	1·8585	5·3605	10·379	15·387	3·4507	70·772	44·197
ϵ	1441·0	198·95	184·76	33·839	27·951	17·429	5·1727	3·4444	0·85238
ΔZ	0·0005	0·0005	0·0005	0·0005	0·0005	0·0008	0·0005	0·0006	0·0006

https://doi.org/10.1017/S0305004100030772 Published online by Cambridge University Press

wave functions, the calculated contribution to $Z(r)$ was taken as the estimate for the next stage. Seven approximations were needed to reduce the maximum difference between the estimated and calculated contributions to $Z(r)$ for the $(4d)^5$ group to 0·001. The other wave functions converged more rapidly.

The results are given in Tables 1 and 2. The maximum difference, ΔZ, between the estimated and calculated values of the contributions to $Z(r)$ for each group are also given in Table 2. It is in no case greater than 0·001.

The author is indebted to Prof. D. R. Hartree for helpful discussion and to Dr M. V. Wilkes for permission to use the facilities of the University Mathematical Laboratory at Cambridge. The work was carried out while the author was maintained by a grant from the Department of Scientific and Industrial Research.

REFERENCES

(1) BLACK, MURIEL M. *Mem. Manchr lit. phil. Soc.* 79 (1935), 29.
(2) GILL, S. *Proc. Camb. phil. Soc.* 47 (1951), 96.
(3) HARTREE, D. R. *Proc. Camb. phil. Soc.* 24 (1928), 89, 111.
(4) HARTREE, D. R. *Proc. roy. Soc.* A, 151 (1935), 96.
(5) RIDLEY, E. C. The interpolation of atomic fields. *Proc. Camb. phil. Soc.* 51 (1955), 693.

THE UNIVERSITY MATHEMATICAL LABORATORY*
CAMBRIDGE

* Present address: Atomic Energy Research Establishment, Harwell.

https://doi.org/10.1017/S0305004100030772 Published online by Cambridge University Press