

Self-consistent field, with exchange, for nitrogen and sodium

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Wave functions for the normal configurations of neutral nitrogen and N^- have been calculated by the method of the self-consistent field with exchange (Fock's equations). To the accuracy of the approximation represented by these equations, the N^- ion would be unstable and liable to auto-ionization, but it is estimated that a better approximation of the treatment of a many-electron atom would give a small positive ionization potential for N^- .

Revised wave functions for Na^+ and the normal state of neutral Na have also been calculated.

Tables of results are given.

[*Note by D.R.H.* At the outbreak of war in September 1939, calculation of wave functions for a number of atoms, carried out by my father (W.H.), had been completed, but the results were still unpublished. Both he and I soon became occupied with other work, and the atomic structure calculations were laid aside. But to avoid the possibility of total loss of these results by enemy action, a copy was sent to Professor J. C. Slater at M.I.T., with a suggestion that he should, if possible, take steps to get them published in the U.S.A. so as to make them generally available. Professor Slater entrusted to Dr Millard F. Manning the preparation of these results for publication, and most of them were published, with some additional results by Manning, in the *Physical Review* (Hartree, Hartree & Manning 1941 *a, b, c*); I would like to take this opportunity of expressing my appreciation of the work of Dr Manning in this connexion. Dr Manning died in 1942, leaving a few of these results still unpublished, and so they remained, since the scientific personnel of the U.S.A., as of Britain, was by then mainly engaged on work more directly related to the allied war effort.

This paper presents the outstanding results for nitrogen (N^- and neutral) and sodium (Na^+). My father died in 1943 so that I have only his note-books to refer to in writing up the results. But the work seems straightforward, with no unusual features, and there is little to do but record the results.

Added in proof. Since writing this paper, I have found among my father's papers some calculations (without exchange) for Au; the results will be published separately.]

1. NITROGEN. WAVE FUNCTIONS

The normal electron configuration of neutral nitrogen (N^0) is $(1s)^2(2s)^2(2p)^3$, giving terms 4S , 2D , 2P in that order (4S deepest); that of N^- is $(1s)^2(2s)^2(2p)^4$ giving 3P , 1D , 1S . Apart from the value of the atomic number, the equations are the same as for singly ionized oxygen and neutral oxygen respectively (Hartree, Hartree

& Swirles 1939, referred to as I). In the present work, superposition of configurations was neglected, so that these equations are obtained by putting $\mu = 0$ in equations (6) and (7) of I. Then, for each of the configurations mentioned, the different states are distinguished by the values of a single coefficient β , which has the following values (see I, table 1):

	N^0			N^-		
β	4S	2D	2P	3P	1D	1S
	$-\frac{3}{5}$	$-\frac{6}{25}$	0	$-\frac{3}{5}$	$-\frac{9}{25}$	0

Results for oxygen (I, § 5) show that the normalized radial wave functions P_N for the different terms arising from a single configuration are nearly linear in β , so for nitrogen the equations have only been solved for the extreme values of β for each configuration. The results are given in table 1. If values of P_N are required for intermediate values of β , they can be obtained by linear interpolation in β .

2. NITROGEN. ENERGY VALUES

The values of the various F and G integrals (see I, § 2) and ϵ -parameters occurring in the expression for the contribution to the energy from the $(2s)(2p)$ shell are given in table 2 (compare I, table 5); the coefficients with which these quantities occur in this expression are given in I, table 2 (column headed E_A ($\mu = 0$)). The values of the ϵ -parameters in table 2 were obtained in the course of the determination of the wave functions; the values of the F and G integrals were calculated from these wave functions. For the intermediate values of β ($-\frac{6}{25}$ for N^0 and $-\frac{9}{25}$ for N^-), values of the F and G integrals and ϵ -parameters were estimated by linear interpolation in β between the values in table 2.

From these quantities, the total energy of the $(2s)(2p)$ shell was calculated; the results are given in table 3. Since the values of some of the F integrals are multiplied by factors up to 8, the third decimal of the individual tabulated values is hardly significant, but it is retained since the calculated *ratio* of the inter-multiplet separations is probably reliable to an accuracy represented by 2 units in this place. Observed values of the ionization energy of the three states of neutral N are given in table 3. No calculated values are available for comparison, since no calculations were carried out for N^+ ; the purpose of including these observed values is to give a comparison between calculated and observed inter-multiplet separations.

The general character of the results for neutral N is very similar to that for O^+ (see I, table 7); the calculated 2D - 4S separation is slightly larger than that observed, whereas the calculated 2P - 2D separation is about 50% larger than that observed, so that the calculated value of the ratio $(^2P-^2D)/(^2D-^4S)$ is 0.68, as compared with the observed value 0.50; to the accuracy of the calculated values, these figures are the same as for O^+ .

The results in table 3 show that, to the accuracy of the approximation on which these calculations are based, the N^- ion is unstable in the sense already defined else-

where (Hartree & Hartree 1938, § 1), namely that it is possible to find a solution to the equations, but the total energy of the configuration is greater than that for the neutral atom, so that the ion would be liable to auto-ionization. However, the calculated energy differences $(N^0, 4S) - (N^-, 3P)$ is only -0.0641 atomic unit, and the results for oxygen suggest that this calculated value is likely to be too low by 0.08 atomic unit and probably more. Hence it seems probable that the lowest state, at least, of N^- is stable; whether the higher states arising from the normal configuration are stable or not is quite uncertain.

These results emphasize the importance of using as good an approximation to the general form of the wave function of a many-electron atom as is practicable, in calculations referring to negative ions. Fock's equations for the self-consistent field with exchange do not form a good enough approximation for the purpose; it is probably necessary explicitly to include in some way the dependence of the wave function on the mutual distances r_{ij} between the electrons, at least between those occupying the outer wave functions such as the $(2p)$ wave functions of O^- or N^- . The development of a means of doing this which leads to a practicable computing process is very much required in this context.

3. SODIUM (Na^+)

Sodium was the first atom for which solutions of Fock's equations were evaluated, this pioneer work being done by Fock & Petrashen (1934). Work on Na^- (Hartree & Hartree 1938) gave results for the core wave functions $[(1s), (2s) \text{ and } (2p)]$ which differed from Fock & Petrashen's wave functions for Na^+ by considerably more than was expected as a result of adding the $(3s)^2$ group to form Na^- , and considerably more, also, than the perturbation of the K^+ core on adding the $(4s)^2$ group to form K^- . Further, the differences between Fock & Petrashen's results for Na^+ and ours for Na^- were rather irregular, and separate examination of the two sets of results traced these irregularities to the Na^+ results.

Fock & Petrashen evaluated the solutions of the inhomogeneous differential equations for the radial wave functions with exchange by a method based on the use of the Green's function. This, while of course formally correct, does not seem the most suitable method for practical computation, and in view of the irregularities already mentioned, it seemed advisable to recalculate Na^+ by straightforward numerical integration. This, it must be emphasized, implies no criticism of Fock & Petrashen's work which, because of its pioneer character, was necessarily done without previous experience of handling these equations, and was a considerable achievement. Since then, however, much experience has been gained in the course of evaluating solutions of these equations for other atoms, and it seemed advisable to revise the results for Na^+ by calculations done in the light of all this experience.

The results are given in table 4, and show only small departures (0.002 at most in P_N) from those for Na^- , though the values of ϵ are considerably different on account of the contribution to the potential, in the region of the core of Na^- , from the $(3s)^2$

group. The differences from Fock & Petrashen's wave functions are, however, quite appreciable, up to 0.017 in $P(2s)$ and 0.014 in $P(2p)$. In view of the discrepancies from Fock & Petrashen's results, the work was done with particular care, and it is believed that the present results are correct to the accuracy of the calculations.

The ($3s$) wave function for Na^0 was also calculated, taking the core wave functions tabulated in table 4; the result is included in table 4. It was found that to secure orthogonality of $P(3s)$ to $P(2s)$ a small but appreciable non-zero value of the non-diagonal parameter $\epsilon_{2s,3s}$ had to be taken ($\epsilon_{2s,3s} = 0.0045$).

Tables of results are given.

TABLE 1. NITROGEN. NORMALIZED WAVE FUNCTIONS

r	neutral N										
	$P(1s)$	$\beta = -\frac{2}{5}$ (4S state)				$\beta = 0$ (2P state)				$P(2s)$	$P(2p)$
		$P(2s)$	$P(2p)$	$P(2s)$	$P(2p)$	$P(2s)$	$P(2p)$	$P(2s)$	$P(2p)$		
0.00	0	0	0	0	0	0	0	0	0	0	
0.01	0.327	0.072	0.0009	0.073	0.0009	0.070	0.0008	0.071	0.0008	0.0008	
0.02	0.611	0.134	0.0037	0.136	0.0036	0.130	0.0032	0.132	0.0031	0.0031	
0.03	0.855	0.187	0.0080	0.190	0.0079	0.182	0.0070	0.184	0.0068	0.0068	
0.04	1.064	0.232	0.0137	0.235	0.0135	0.225	0.0120	0.228	0.0117	0.0117	
0.06	1.389	0.300	0.029	0.304	0.0285	0.291	0.025	0.294	0.024 ₅	0.024 ₅	
0.08	1.615	0.343	0.048	0.347	0.047 ₅	0.333	0.042	0.336	0.041	0.041	
0.10	1.761	0.365	0.070 ₅	0.370	0.069 ₅	0.355	0.061 ₅	0.359	0.060	0.060	
0.12	1.845	0.371	0.095 ₅	0.376	0.094	0.360	0.083	0.364	0.081 ₅	0.081 ₅	
0.14	1.880	0.363	0.122	0.368	0.120 ₅	0.353	0.106	0.357	0.104	0.104	
0.16	1.878	0.344	0.150	0.349	0.148	0.334	0.131	0.338	0.128	0.128	
0.18	1.848	0.316	0.179	0.320	0.176 ₅	0.307	0.156	0.310	0.153	0.153	
0.20	1.797	0.281	0.209	0.285	0.206	0.273	0.182	0.276	0.178	0.178	
0.25	1.613	0.172	0.283	0.174	0.279	0.168	0.247	0.169	0.242	0.242	
0.30	1.393	0.047	0.356	0.047	0.350	0.046	0.310	0.046	0.304	0.304	
0.35	1.173	-0.083	0.425	-0.084	0.417	-0.080	0.370	-0.081	0.363	0.363	
0.40	0.969	-0.210	0.488	-0.212	0.479	-0.203	0.426	-0.205	0.417	0.417	
0.45	0.789	-0.328	0.546	-0.332	0.535	-0.318	0.476	-0.321	0.467	0.467	
0.50	0.636	-0.436	0.597	-0.441	0.585	-0.423	0.521	-0.427	0.511	0.511	
0.6	0.404	-0.614	0.680	-0.621	0.665	-0.595	0.595	-0.602	0.582	0.582	
0.7	0.250	-0.742	0.739	-0.750	0.722	-0.720	0.649	-0.728	0.634	0.634	
0.8	0.153	-0.826	0.776	-0.833	0.758	-0.803	0.684	-0.811	0.668	0.668	
0.9	0.092	-0.872	0.795	-0.878	0.776	-0.849	0.706	-0.856	0.689	0.689	
1.0	0.055	-0.889	0.800	-0.894	0.781	-0.867	0.715	-0.874	0.698	0.698	
1.1	0.033	-0.884	0.793	-0.888	0.775	-0.864	0.715	-0.870	0.698	0.698	
1.2	0.019	-0.862	0.777	-0.865	0.761	-0.846	0.708	-0.850	0.690	0.690	
1.4	0.007	-0.788	0.727	-0.788	0.717	-0.780	0.679	-0.782	0.663	0.663	
1.6	0.003	-0.694	0.663	-0.692	0.659	-0.695	0.638	-0.693	0.624	0.624	
1.8	0.001	-0.597	0.595	-0.593	0.596	-0.606	0.592	-0.602	0.582	0.582	
2.0	—	-0.505	0.527	-0.499	0.534	-0.520	0.545	-0.515	0.538	0.538	
2.2	—	-0.422	0.461	-0.415	0.473	-0.442	0.498	-0.436	0.496	0.496	
2.4	—	-0.349	0.401	-0.342	0.417	-0.374	0.455	-0.366	0.456	0.456	
2.6	—	-0.286	0.346	-0.280	0.366	-0.314	0.414	-0.306	0.418	0.418	
2.8	—	-0.233	0.297	-0.228	0.320	-0.263	0.376	-0.255	0.383	0.383	
3.0	—	-0.189	0.254	-0.184	0.278	-0.220	0.342	-0.211	0.352	0.352	

TABLE 1 (cont.)

<i>r</i>	neutral N					N ⁻			
	<i>P</i> (1 <i>s</i>)	$\beta = -\frac{3}{8}$ (⁴ S state)		$\beta = 0$ (² P state)		$\beta = -\frac{3}{8}$ (³ P state)		$\beta = 0$ (¹ S state)	
		<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)
3.2	—	-0.154	0.216	-0.149	0.241	-0.183	0.310	-0.175	0.323
3.4	—	-0.123	0.184	-0.119	0.208	-0.153	0.282	-0.145	0.296
3.6	—	-0.099	0.156	-0.095	0.180	-0.127	0.256	-0.120	0.272
3.8	—	-0.079	0.132	-0.076	0.155	-0.106	0.232	-0.100	0.250
4.0	—	-0.063	0.111	-0.060	0.133	-0.088	0.210	-0.083	0.230
4.5	—	-0.036	0.072	-0.034	0.090	-0.055	0.166	-0.052	0.189
5.0	—	-0.020	0.046	-0.019	0.060	-0.034	0.131	-0.032	0.155
5.5	—	-0.011	0.030	-0.011	0.040	-0.021	0.103	-0.020	0.127
6.0	—	-0.006	0.019	-0.006	0.026	-0.013	0.082	-0.013	0.105
6.5	—	-0.003	0.012	-0.003	0.017	-0.008	0.065	-0.008	0.087
7.0	—	-0.002	0.008	-0.002	0.011	-0.005	0.052	-0.005	0.072
8	—	—	0.003	—	0.005	-0.002	0.033	-0.002	0.049
9	—	—	0.001	—	0.002	-0.001	0.021	-0.001	0.034
10	—	—	—	—	0.001	—	0.013	—	0.024
11	—	—	—	—	—	—	0.008	—	0.016
12	—	—	—	—	—	—	0.005	—	0.011
14	—	—	—	—	—	—	0.002	—	0.005
16	—	—	—	—	—	—	0.001	—	0.002
18	—	—	—	—	—	—	—	—	0.001

 TABLE 2. NITROGEN. *F* AND *G* INTEGRALS AND ϵ VALUES

β	N ⁰		N ⁻	
	⁴ S	² P	³ P	¹ S
	$-\frac{3}{8}$	0	$-\frac{3}{8}$	0
<i>F</i> ₀ (2 <i>s</i> , 2 <i>s</i>)	0.685	0.690	0.659	0.666
<i>F</i> ₀ (2 <i>s</i> , 2 <i>p</i>)	0.668	0.658	0.594	0.583
<i>F</i> ₀ (2 <i>p</i> , 2 <i>p</i>)	0.655	0.630	0.542	0.518
<i>F</i> ₂ (2 <i>p</i> , 2 <i>p</i>)	0.294	0.280	0.231	0.217
<i>G</i> ₁ (2 <i>s</i> , 2 <i>p</i>)	0.410	0.401	0.354	0.344
$\epsilon_{2s, 2s}$	1.890	1.958	1.161	1.250
$\epsilon_{2p, 2p}$	1.126	0.941	0.187	0.107

TABLE 3. NITROGEN. ENERGIES

N ⁰		calculated total energy of (2 <i>s</i>) (2 <i>p</i>) shell		observed ionization energy	
N ⁰	⁴ S	-9.651	92	0.535	88
	² D	-9.559	63	0.447	44
	² P	-9.496		0.403	
N ⁻	³ P	-9.587	54		
	¹ D	-9.533	89		
	¹ S	-9.444			

TABLE 4. SODIUM. NORMALIZED WAVE FUNCTIONS

Na ⁺				Na ⁰	Na ⁺				Na ⁰
<i>r</i>	<i>P</i> (1 <i>s</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)	<i>r</i>	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)	
0.00	0	0	0	0	3.2	-0.013	0.035	0.508	
0.01	0.629	0.154	0.004	0.023	3.4	-0.009	0.026	0.510	
0.02	1.128	0.274	0.014	0.041	3.6	-0.006	0.019	0.508	
0.03	1.517	0.366	0.030	0.055	3.8	-0.004	0.014	0.502	
0.04	1.814	0.433	0.050	0.065	4.0	-0.002 _s	0.010	0.493	
0.06	2.192	0.507	0.102	0.076	4.5	-0.001	0.004 _s	0.458	
0.08	2.356	0.517	0.163	0.077	5.0	—	0.002	0.414	
0.10	2.377	0.481	0.231	0.071	5.5	—	0.001	0.366	
0.12	2.305	0.412	0.302	0.060	6.0	—	0.000 _s	0.318	
0.14	2.175	0.320	0.374	0.046	6.5	—	—	0.272	
0.16	2.012	0.215	0.444	0.030	7.0	—	—	0.230	
0.18	1.834	0.102	0.512	0.013	7.5	—	—	0.192	
0.20	1.652	-0.015	0.578	-0.005	8.0	—	—	0.160	
0.25	1.227	-0.301	0.724	-0.049	9	—	—	0.108	
0.30	0.878	-0.555	0.842	-0.087	10	—	—	0.072	
0.35	0.614	-0.763	0.933	-0.117	11	—	—	0.047	
0.40	0.422	-0.923	0.997	-0.138	12	—	—	0.030	
0.45	0.287	-1.037	1.039	-0.152	13	—	—	0.019	
0.50	0.194	-1.112	1.061	-0.158	14	—	—	0.012	
0.6	0.088	-1.169	1.061	-0.153	16	—	—	0.005	
0.7	0.040	-1.139	1.021	-0.131	18	—	—	0.002	
0.8	0.018	-1.061	0.956	-0.097	20	—	—	0.001	
0.9	0.008	-0.958	0.880	-0.058					
1.0	0.003	-0.846	0.799	-0.015					
1.1	0.001	-0.736	0.718	+0.028					
1.2	—	-0.632	0.640	0.072					
1.4	—	-0.455	0.501	0.156					
1.6	—	-0.319	0.385	0.232					
1.8	—	-0.220	0.292	0.297					
2.0	—	-0.149	0.219	0.354					
2.2	—	-0.101	0.163	0.400					
2.4	—	-0.068	0.121	0.437					
2.6	—	-0.045	0.089	0.466					
2.8	—	-0.030	0.065	0.487					
3.0	—	-0.020	0.048	0.501					
					$\epsilon_{nl, nl}$	81.46	6.15 ₀	3.60 ₃	0.361
						Na ⁺			Na ⁰
						<i>P</i> (1 <i>s</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)
					<i>r</i>	<i>r</i>	<i>r</i>	<i>r</i> ²	<i>r</i>
					0.00	70.25	17.16	38.92	2.57 _s
					0.01	62.94	15.36	36.85	2.30 _s
					0.02	56.41	13.71	34.91	2.06
					0.03	50.57	12.21	33.09	1.83
					0.04	45.35	10.84	31.38	1.62

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