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Fock Self-Consistent Field in the Three-Configuration Approximation for the Beryllium Atom

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The problem of the practical application of the Fock self-consistent field method in the many-configuration approximation is examined. The three-configuration approximation $1s^22s^2 - 1s^22p^2 - 2s^22p^2$ is applied to the ground configuration of the neutral beryllium atom. Values of the total potential function and the radial probability distribution are given.

1. INTRODUCTION

THE Fock self-consistent field method[1] was extended to the many-configuration approximation in reference 2. It was shown[3] that the solution of the Fock equations in the two-configuration approximation is practically feasible. It was later shown[4] that the solutions of the Fock equations in the two-configuration approximation can, without noticeable loss of accuracy, be replaced by solutions of simplified Fock equations in the two-configuration approximation. Computations by this simplified method were carried out for the ground configurations of Be, B$^+$, C^{++} [4], and B [5].

The fact that going over from the one-configuration to the two-configuration approximation involves relatively little additional computational labor points to the possibility of practical extension of the method to the case where a greater number of configurations are taken into account. The present paper is devoted to this question. We solve the problem by a method similar to one previously applied[6], in which analytic wave functions were used. Calculations are carried out for the ground configuration of the neutral beryllium atom.

Previous work[6] shows that in the case of the three-configuration approximation $1s^22s^2 - 1s^22p^2 - 1s^23d^2$, the last configuration gives a negligible effect. This configuration was therefore neglected in references 3 and 4, and the two-configuration approximation $1s^22s^2 - 1s^22p^2$ applied. Further study of the question shows that, for the ground configuration of atoms of the type of Be, when one uses one-electron wave functions determined in the many-configuration-approximation, one should use the three-configuration approximation $1s^22s^2 - 1s^22p^2 - 2s^22p^2$ for more accurate calculations. So, as a specific example of the application of the Fock self-consistent field method in the many-configuration approximation, we have in the present paper applied the last-mentioned three-configuration approximation for the case of the Be atom.

2. GENERAL CONSIDERATION OF THE PROBLEM

As in reference 6, the configuration under investigation will be denoted by the subscript 1. We shall assume that the many-configuration approximation reduces, for practical purposes, to the m - configuration approximation. Formulas (2.1) - (2.8) of reference 6 are unaltered, so that to avoid repetition we shall not give them here.

In order to apply the Fock method for finding one-electron wave functions, we construct the expression:

$$E' = \frac{1}{\sum\limits_{i=1}^{m} a_{1i}^2}\left[\sum_{i=1}^{m} a_{1i}^2 E'_{ii} + 2\sum_{k>i=1}^{m} a_{1i}\, a_{1k}\, E'_{ik}\right], \quad (2.1)$$

where

$$E'_{ik} = E_{ik} + \sum_{nl,\, n'l} (1 + \delta_{ik}\,\delta_{nn'} - \delta_{nn'}) \quad (2.2)$$
$$\times\ a_{1i}\, a_{1k}\, \varepsilon_{(nl,\, n'l)_{ik}}\, N(nl,\ n'l)_{ik}.$$

Here δ_{ij} is the Kronecker delta, $\epsilon_{(nl,n'l)_{ik}}$ are

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[1] V. A. Fock, Z. Physik. 61, 126 (1930).

[2] A. P. Iutsis, J. Exper. Theoret. Phys. USSR 23, 129 (1952).

[3] V. V. Kibartas and A. P. Iutsis, J. Exper. Theoret. Phys. USSR 25, 264 (1953).

[4] A. P. Iutsis, V. V. Kibartas and I. I. Glembotskii, J. Exper. Theoret. Phys. USSR 27, 425 (1954).

[5] I. I. Glembotski, V. V. Kibartas and A. P. Iutsis, J. Exper. Theoret. Phys. USSR 29, 617 (1955); Soviet Phys. 2, 476 (1956).

[6] V. I. Kavetskis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR 25, 257 (1953).

Lagrange multipliers, $N(nl, n'l)_{ik}$ is defined by expression (2.8) of reference 6, and the summation extends over all nl and $n'l$ (including $n' = n$) for given i and k.

We shall assume that the E_{ik} are expressed in terms of radial integrals. Then the Fock equations in the many-configuration approximation take on the following quite general form:

$$\frac{\partial E'_{11}}{\partial P_1(nl\,|\,r)} + 2\sum_{i=2}^{m} a_{1i}\,\frac{\partial E'_{1i}}{\partial P_1(nl\,|\,r)} = 0 \qquad (2.3a)$$

for all nl of the configuration under investigation, and

$$\frac{\partial E'_{kk}}{\partial P_k(nl\,|\,r)} + 2\sum_{k\neq j=1}^{m} \frac{a_{1j}}{a_{1k}}\,\frac{\partial E'_{kj}}{\partial P_k(nl\,|\,r)} = 0 \qquad (2.3b)$$

for all nl of the perturbing configurations ($k = 2,3,\ldots m$).

The first term in Eq. (2.3) is just the left-hand side of the usual Fock equations (in the one-configuration approximation), while the remaining terms are configuration terms. We should point out that configuration terms appear in the equations of only those $P(nl\,|\,r)$ which are contained in at least one of the $E_{ij}(i \neq j = 1,2,\ldots m)$. The remaining equations are just the corresponding ordinary Fock equations.

We consider the case where the perturbing configurations differ from the fundamental configuration in a pair of (nl)'s. Then the symbolic derivative of E'_{ik} for $k \neq i$ is an exchange term multiplied by the factor $N(nl,n'l)_{ik} \leq 1$. Since $a_{1i} < 1$ for all i, the configuration terms in Eq. (2.3a) are insignificant compared to the exchange terms and can be neglected. On the other hand, in those equations (2.3b) in which configuration terms appear, the term in the sum for $j = 1$ is dominant, since it contains the factor $1/a_{ik}$ (note that $a_{11} = 1$). The other terms are less important. We can therefore neglect them relative to the dominant term. Under these conditions, the equations (2.3b) break up into equations for the separate two-configuration approximations $1 - k$ (for $k = 2,3,\ldots m$). In this simplified form of the Fock self-consistent field method in the many-configuration approximation, we use solutions of the ordinary Fock equations as one-electron wave functions for the fundamental configuration, and solutions of the Fock equations in the various two-configuration approximations as one-electron wave functions for the perturbing configurations. In these separate two-configuration approximations, we can make the further simplification, as proposed in reference 4 and applied in references 4 and 3: the exchange terms are neglected compared to configuration terms in the Fock equations for the wave functions of the perturbing configurations.

For those wave functions of the perturbing configuration whose Fock equations do not contain configuration terms, the corresponding one-electron wave functions of the fundamental configuration are used. Thus, in practical application of the Fock self-consistent field in the many-configuration approximation, in addition to solving the ordinary Fock equations for the fundamental configuration, it is sufficient to solve the simplified two-configuration Fock equations for those wave functions of the perturbing configurations which appear in the expressions for the nondiagonal matrix elements of the energy, which couple the fundamental configuration with the corresponding perturbing configurations.

3. PRACTICAL APPLICATION OF THE METHOD

Let us apply the self-consistent Fock field in the three-configuration approximation $1s^2 2s^2 - 1s^2 2p^2 - 2s^2 2p^2$ (abbreviated 1 - 2 - 3) to the ground configuration of the beryllium atom. In this case, the nondiagonal matrix elements of the energy are:

$$E_{12} = -\frac{1}{\sqrt{3}}\,G_1(2s,\,2p)_{12}N^2(1s,\,1s)_{12}, \qquad (3.1)$$

$$E_{13} = -\frac{1}{\sqrt{3}}\,G_1(1s,\,2p)_{13}N^2(2s,\,2s)_{13}, \qquad (3.2)$$

$$E_{23} = G_0(1s,\,2s)_{23}N^2(2p,\,2p)_{23}. \qquad (3.3)$$

We assume that

$$P_2(1s\,|\,r) = P_1(1s\,|\,r) = P(1s\,|\,r), \qquad (3.4a)$$

$$P_3(2s\,|\,r) = P_1(2s\,|\,r) = P(2s\,|\,r). \qquad (3.4b)$$

Here the indices attached to a function denote the configuration to which the corresponding radial wave function refers. Functions without indices are those of the fundamental configuration, determined in the one-configuration approximation. In view of Eq. (3.4), we have

$$N(1s,\,1s)_{12} = N(2s,\,2s)_{13} = 1. \qquad (3.5)$$

We have the following simplified two-configuration equations for determining the functions $P_2(2p\,|\,r)$ and $P_3(2p\,|\,r)$:

$$\left[\frac{d^2}{dr^2}+\frac{2Z-4Y_0(1s,\,1s\,|\,r)-2Y_0(2p,\,2p\,|\,r)_{22}-0{,}8Y_2(2p,\,2p\,|\,r)_{22}}{r}-\frac{2}{r^2}\right.$$
$$\left.-\varepsilon_{(2p,\,2p)_{22}}\right]P_2(2p\,|\,r)+\frac{1}{a_{12}}\frac{2}{\sqrt{3}}\frac{Y_1(2s,\,2p\,|\,r)_{12}}{r}P(2s\,|\,r)=0, \tag{3.6a}$$

$$\left[\frac{d^2}{dr^2}+\frac{2Z-4Y_0(2s,\,2s\,|\,r)-2Y_0(2p,\,2p\,|\,r)_{33}-0{,}8Y_2(2p,\,2p\,|\,r)_{33}}{r}-\frac{2}{r^2}\right.$$
$$\left.-\varepsilon_{(2p,\,2p)_{33}}\right]P_3(2p\,|\,r)+\frac{1}{a_{13}}\frac{2}{\sqrt{3}}\frac{Y_1(1s,\,2p\,|\,r)_{13}}{r}P(1s\,|\,r)=0. \tag{3.6b}$$

The values of the functions $P(1s\,|r)$ and $P(2s|r)$ are given in reference 3. For the function $P_2(2p|r)$ we use the corresponding function, given in reference 3, which is a solution of the unsimplified equation in the two-configuration approximation. The solution of Eq. (3.6b) is given in Table I. An analytic wave function was used for starting the solution of this equation. The solution was carried to self-consistency index 0.0050 for $P_3(2p|r)$ and 0.0005 for a_{13}.

TABLE I

Normalized Radial Wave Function $P(2p|r)$ of the Perturbing Configuration $2s^2 2p^2$ of the Two-Configuration Approximation $1s^2 2s^2$-$2s^2 2p^2$

r	$P(2p\|r)$	r	$P(2p\|r)$	r	$P(2p\|r)$
0.00	0.0000	0.30	1.4396	1.10	0.2093
0.01	0.0051	0.32	1.4761	1.15	0.1727
0.02	0.0201	0.34	1.4993	1.20	0.1422
0.03	0.0441	0.36	1.5104	1.25	0.1168
0.04	0.0764	0.38	1.5103	1.30	0.0957
0.05	0.1161	0.40	1.5003	1.35	0.0783
0.06	0.1623	0.42	1.4815	1.40	0.0640
0.07	0.2142	0.44	1.4551	1.45	0.0522
0.08	0.2708	0.46	1.4222	1.50	0.0426
0.09	0.3313	0.48	1.3840	1.55	0.0347
0.10	0.3949	0.50	1.3414		
0.11	0.4606	0.52	1.2953	1.6	0.0283
0.12	0.5279	0.54	1.2467	1.7	0.0187
0.13	0.5959	0.56	1.1961	1.8	0.0124
0.14	0.6640	0.58	1.1443	1.9	0.0083
0.15	0.7316	0.60	1.0919	2.0	0.0055
0.16	0.7981	0.65	0.9612	2.1	0.0037
0.17	0.8631	0.70	0.8357	2.2	0.0024
0.18	0.9261	0.75	0.7191	2.3	0.0016
0.19	0.9868	0.80	0.6133	2.4	0.0011
0.20	1.0447	0.85	0.5193	2.5	0.0007
0.22	1.1516	0.90	0.4370	2.6	0.0005
0.24	1.2452	0.95	0.3658	2.7	0.0003
0.26	1.3246	1.00	0.3049	2.8	0.0002
0.28	1.3893	1.05	0.2530	3.0	0.0001

The values of the Lagrange multipliers, radial integrals and energy are given in Table II. To obtain the value of the energy in the three-configuration approximation, we also made use of the data of Table 2 of reference 3.

4. TOTAL POTENTIAL FUNCTION AND RADIAL PROBABILITY DISTRIBUTION

The total potential function[4] has the following form in the three-configuration approximation $1s^2 2s^2$ - $1s^2 2p^2$ - $2s^2 2p^2$:

$$T(r)=2\left\{Z-\frac{1}{1+a_{12}^2+a_{13}^2}\left[2(1+a_{12}^2)\,Y_0(1s,\,1s\,|\,r)\right.\right.$$
$$\left.\left.+2(1+a_{13}^2)\,Y_0(2s,2s\,|\,r)+2a_{12}^2Y_0(2p,2p\,|\,r)_{22}+2a_{13}^2Y_0(2p,\,2p\,|\,r)_{33}\right]\right\}. \tag{4.1}$$

TABLE II

Values of Radial Integrals and Energy (in atomic units)

$\varepsilon(2p, 2p)_{33} = 33{,}936$
$F_0(2p, 2p)_{33} = 2{,}0060$
$F_2(2p, 2p)_{33} = 1{,}0012$
$F_0(2s, 2p)_{33} = 0.4752$
$G_1(2s, 2p)_{33} = 0{,}0168$

$G_1(1s, 2p)_{13} = 1{,}2570$
$N(2p, 2p)_{23} = 0{,}1837$
$E_{33} = +9{,}197$
$E_{13} = -0{,}726$
$E_{23} = 0{,}001$

	a	b
ΔE	-0.022	-0.065
a_{13}	$+0.030$	$+0.030$
a_{12}	$+0.33$	$+0.31_5$
E_{theor}		-14.642
E_{exp}		-14.666

Footnote.- a) two-configuration approximation $1s^2 2s^2$- $2s^2 2p^2$; b) three-configuration approximation $1s^2 2s^2$- $1s^2 2p^2$- $2s^2 2p^2$.

TABLE III

Total Potential Function and Radial Probability Distribution

r	$T(r)$	$10^3\delta T$	W	$10^3\delta W$	r	$T(r)$	$10^3\delta T$	W	$10^3\delta W$
0.00	8.000	0	0.000	0	1.0	2.205	−8	0.514	+10
0.02	7.665	0	0.151	−1	1.1	2.033	−8	0.487	+ 8
0.04	7.337	+1	0.516	−2	1.2	1.869	−8	0.506	+ 7
0.06	7.018	+1	0.991	−3	1.3	1.714	−8	0.547	+ 5
0.08	6.712	+1	1.504	−5	1.4	1.568	−8	0.599	+ 4
0.10	6.421	+1	2.010	−6	1.5	1.430	−8	0.651	+ 2
0.12	6.146	+1	2.476	−8	1.6	1.300	−8	0.698	+ 2
0.14	5.887	+1	2.886	−9	1.8	1.067	−8	0.765	+ 1
0.16	5.645	+1	3.230	−10	2.0	0.868	−7	0.792	+ 1
0.18	5.420	+1	3.507	−11	2.2	0.700	−7	0.784	+ 1
0.20	5.209	+1	3.712	−12	2.4	0.561	−7	0.748	+ 1
0.24	4.833	0	3.945	−10	2.6	0.447	−6	0.693	+ 1
0.28	4.509	0	3.969	−8	2.8	0.355	−5	0.628	+ 1
0.32	4.231	−1	3.841	−6	3.2	0.219	−5	0.488	0
0.36	3.992	−1	3.608	−3	3.6	0.134	−3	0.358	− 2
0.40	3.784	−2	3.312	0	4.0	0.081	−3	0.253	− 3
0.44	3.603	−3	2.984	+2	4.4	0.049	−1	0.173	− 3
0.48	3.443	−4	2.650	+4	4.8	0.029	−1	0.116	− 2
0.52	3.301	−4	2.325	+6	5.2	0.017	−1	0.076	− 2
0.56	3.174	−5	2.021	+8	5.6	0.010	0	0.049	− 2
0.6	3.059	−5	1.745	+10	6	0.006	0	0.031	− 1
0.7	2.806	−6	1.189	+11	7	0.002_2	0	0.010	0
0.8	2.588	−7	0.824	+11	8	0.000_4	0	0.003	0
0.9	2.388	−8	0.614	+12	9			0.001	0

Footnote.- The values of T and W are given in the three-configuration approximation $1s^2 2s^2$ - $1s^2 2p^2$ - $2s^2 2p^2$. Also given are the differences (three-config. value minus one-config. value) multiplied by 1 000.

For the radial distribution we find:

$$W(r) = \frac{1}{1 + a_{12}^2 + a_{13}^2} [2(1 + a_{12}^2) P^2(1s \mid r) + 2(1 + a_{13}^2) P^2(2s \mid r) + 2a_{12}^2 P_2^2(2p \mid r) + 2a_{13}^2 P_3^2(2p \mid r)]. \tag{4.2}$$

Equation (3.4) was used in getting Eqs. (4.1) and (4.2).

The values of T and W are presented in Table III. The intervals in the table have been doubled for the same reason that applied to the corresponding table of reference 5.

5. CONCLUSIONS

Comparison of Table I of the present paper with Table I of reference 3 shows that the function $P(2p|r)$ for the perturbing configuration $2s^2 2p^2$ deviates from the function $P(2p|r)$ for the perturbing configuration $1s^2 2p^2$, approaching the function $P(1s|r)$. This results from the smallness of a_{13} in (3.6b). This unusual behavior of the $P(2p|r)$ function when calculated in the two-configuration approximation is the reason why the energy correction caused by the perturbing configuration $2s^2 2p^2$ is significant, whereas it is negligible if we use one-electron wave functions determined in the one-configuration approximation.

From Table II we see that the three-configuration approximation $1s^2 2s^2$ - $1s^2 2p^2$ - $2s^2 2p^2$ gives a correction to the energy of 0.064 atomic units. The energy value calculated in the three-configuration approximation deviates from the experimental value by only 0.024 atomic units.

Table III shows that the absolute magnitudes of the differences between the values of the total potential function T and the probability distribution W determined in the three-configuration approximation and their values as given by the one-configuration approximation are no greater than 0.008 and 0.012 respectively. Most of the change is due to the perturbing configuration $1s^2 2p^2$, while the configuration $2s^2 2p^2$, because of the smallness of a_{13}, has a negligible effect on these quantities.

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