

Note on Fock Equations for Complex Configurations

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Fock's equations for a general atomic state are written in terms of the coefficients of Slater's F 's and G 's in the energy of that state. With the special formulas which are given to take care of the closed shells, this enables the Fock equations to be written down immediately for any desired state. For a complex configuration, in order to obtain *one* particular set of radial factors to use as a basis for a first-order perturbation calculation, a process is given for obtaining that set of radial factors for which the center of gravity of the configuration is a minimum, for any coupling. Finally, it is shown how equations may be obtained for finding the best radial factors with which to form the eigenfunctions of a *given term* of a configuration in LS coupling, and suggested that this may be made the basis of a perturbation theory in which the different types of terms are considered independently.

FOCK¹ has given equations which determine the radial factors of the one-electron functions (orbitals) which minimize the energy for an antisymmetric atomic state characterized by a given set of one-electron quantum numbers (orbits). These equations give functions which are superior to Hartree's because they take account of the exchange terms in the matrix elements of the Hamiltonian. Fock and Petraschen² have developed a practical, though necessarily laborious, method for numerical solution of these equations, and have in this way calculated the energy levels of the valence electron of Na and Li in the field of Na⁺ and Li⁺, respectively, with very good experimental agreement.

These radial factors minimize the diagonal element of the Hamiltonian (with magnetic interactions neglected) for a given state of the atom specified by a given set of electronic orbits. In a complex configuration, the actual eigenfunctions are not characterized in this way, but are linear combinations of such states characterized by values of resultant angular momenta. The equations as given by Fock may be used for configurations with only closed shells, with just one electron outside of closed shells, or with just one electron missing from closed shells;³ but require modification for configurations giving rise to more than one term in LS coupling.

We shall here discuss the question of the equa-

¹ Fock, *Zeits. f. Physik* **61**, 126; **62**, 795 (1930); **81**, 195 (1933).

² Fock and Petraschen, *Phys. Zeits. Sowjetunion* **6**, 368 (1934); **8**, 547 (1935).

³ Equations for fluorine $1s^2 2s^2 2p^5$ are given by Brown, *Phys. Rev.* **44**, 214 (1933). Our mode of approach to the Fock equations resembles that used by Brown.

tions to be solved in the case of atoms with any number of valence electrons, using $1s^2 2s^2 2p^2$ as illustration.

We first sketch a simple general derivation of Fock's equations, obtaining them in a form which is particularly convenient to specialize to any particular case.⁴

Consider a particular state of an N electron atom, formed by taking an antisymmetric linear combination of orbitals of the type $r^{-1}R(n^i l^i) \Theta(l^i m_l^i) \Phi(m_l^i) \delta(\sigma, m_s^i)$ with definite assigned quantum numbers $n^i l^i m_l^i m_s^i$ ($i=1, 2, \dots, N$). Let the state in question belong to a configuration in which P different shells I, II, \dots , P occur, with shell I containing η^I electrons, shell II, η^{II} electrons, etc. Then the state is completely determined except for the P radial factors $R(I), R(II), \dots, R(P)$, for which only the numbers of nodes [$n^K - l^K - 1$ in $R(K)$] are specified. The diagonal element of the Hamiltonian for this state is easily obtained by Slater's method in the form

$$\sum_{K=I}^P \eta^K \int_{r=0}^{\infty} R(K) O^K R(K) + \sum_{J \geq K=I}^P \sum_{\kappa} [A^{\kappa}(JK) F^{\kappa}(J, K) + B^{\kappa}(JK) G^{\kappa}(J, K)], \quad (1)$$

where O^K is the operator

$$O^K = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{l^K(l^K+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r},$$

⁴ The theory prerequisite to these considerations will be found in detail in Chapters V, VI, VII of Condon and Shortley, *Theory of Atomic Spectra* (Cambridge, 1935). We follow the notation of this book.

$A^k(\text{JK})$ and $B^k(\text{JK})$ are numerical coefficients (symmetrical in J and K), and F^k and G^k are certain radial integrals:

$$F^k(\text{J}, \text{K}) = e^2 \int_{r_1} \int_{r_2} R_1^2(\text{J}) R_2^2(\text{K}) r_{<}^k / r_{>}^{k+1},$$

$$G^k(\text{J}, \text{K}) = e^2 \int_{r_1} \int_{r_2} R_1(\text{J}) R_1(\text{K}) R_2(\text{J}) R_2(\text{K}) r_{<}^k / r_{>}^{k+1},$$

where $r_{<}$ is the lesser, $r_{>}$ the greater, of r_1 and r_2 . Expression (1) is correct only if all radial factors are normal and those of the same l value are orthogonal. In order to permit satisfaction of these requirements, we minimize

$$(1) - \sum_{\text{K}=\text{I}}^{\text{P}} \delta(l^{\text{J}}, l^{\text{K}}) \lambda^{\text{JK}} \int_{r=0}^{\infty} R(\text{J}) R(\text{K}), \quad (2)$$

where the λ 's are Lagrange multipliers ($\lambda^{\text{JK}} = \lambda^{\text{KJ}}$). Equating to zero the coefficient of $2\delta R(\text{M})$ in the variation of this expression, which is very easy to calculate, we obtain

$$\eta^{\text{M}} O^{\text{M}} R(\text{M}) + \sum_{\text{K}=\text{I}}^{\text{P}} (1 + \delta^{\text{KM}}) \sum_{\text{K}} [A^k(\text{MK}) \times T^k(\text{KK}) R(\text{M}) + B^k(\text{MK}) T^k(\text{MK}) R(\text{K})]$$

$$= \sum_{\text{K}=\text{I}}^{\text{P}} \delta(l^{\text{K}}, l^{\text{M}}) \lambda^{\text{MK}} R(\text{K}), \quad (3)$$

where $T^k(\text{MK})$ is the following function of the radius r :

$$T_{r^k}(\text{MK}) = e^2 \int_{r'=0}^{\infty} R_{r'}(\text{M}) R_{r'}(\text{K}) r_{<}^k / r_{>}^{k+1}. \quad (4)^5$$

When (3) is written successively for $\text{M}=\text{I}, \dots, \text{P}$, it gives the system of P simultaneous integro-differential equations (*Fock equations*) to be solved for the P radial factors. On multiplying (3) by $R(\text{M})$, integrating over r and summing over M , we find that the diagonal matrix component (1) is given by

$$\frac{1}{2} \sum_{\text{M}} \left[\lambda^{\text{MM}} + \eta^{\text{M}} \int R(\text{M}) O^{\text{M}} R(\text{M}) \right]. \quad (5)$$

⁵ This function Fock calls $(2\kappa+1)F_{\kappa}^{\text{MK}}$. We use T to avoid confusion with Slater's F, G, H, I, J, K —all of frequent occurrence in central-field theory.

General formulas may be obtained for the coefficients A^k, B^k of (1) which involve a closed shell (§ 9, Chapter VI, of Condon and Shortley⁴) so that (3) may be immediately reduced to a form involving only A 's and B 's referring to pairs of incomplete shells. Let the configuration contain $\text{P}-\text{Q}$ complete shells and Q incomplete shells. If the shell M is complete [$\eta^{\text{M}} = 2(2l^{\text{M}} + 1)$], (3) becomes

$$\eta^{\text{M}} \left[O^{\text{M}} + \sum_{\text{K}=\text{I}}^{\text{P}} \eta^{\text{K}} T^0(\text{KK}) \right] R(\text{M})$$

$$- \frac{1}{4} \eta^{\text{M}} \sum_{\text{K}=\text{I}}^{\text{P}} \eta^{\text{K}} \sum_{\kappa} C(l^{\text{M}}, l^{\text{K}}, \kappa) T^{\kappa}(\text{MK}) R(\text{K})$$

$$= \sum_{\text{K}=\text{I}}^{\text{P}} \delta(l^{\text{K}}, l^{\text{M}}) \lambda^{\text{KM}} R(\text{K}). \quad (6)^6$$

We see from this equation that we may set the λ^{KM} connecting any two different closed shells equal to zero, since the radial factors of two closed shells of the same l value are eigenfunctions of the same Hermitian operator, that on the left side of (6), and are therefore automatically orthogonal. This has been noted by Fock.¹

If the shell M is one of the Q incomplete shells, (3) becomes

$$\eta^{\text{M}} \left[O^{\text{M}} + \sum_{\text{K}=\text{I}}^{\text{P}-\text{Q}} \eta^{\text{K}} T^0(\text{KK}) \right] R(\text{M})$$

$$- \frac{1}{4} \eta^{\text{M}} \sum_{\text{K}=\text{I}}^{\text{P}-\text{Q}} \eta^{\text{K}} \sum_{\kappa} C(l^{\text{M}}, l^{\text{K}}, \kappa) T^{\kappa}(\text{MK}) R(\text{K})$$

$$+ \sum_{\text{K} \subset \text{Q}} (1 + \delta^{\text{KM}}) \sum_{\text{K}} [A^k(\text{MK}) T^k(\text{KK}) R(\text{M}) + B^k(\text{MK}) T^k(\text{MK}) R(\text{K})]$$

$$= \sum_{\text{K}=\text{I}}^{\text{P}} \delta(l^{\text{K}}, l^{\text{M}}) \lambda^{\text{KM}} R(\text{K}). \quad (7)$$

Here $\text{K} \subset \text{Q}$ indicates that K runs over the Q incomplete shells $\text{P}-\text{Q}+\text{I}, \text{P}-\text{Q}+\text{II}, \dots, \text{P}$,

⁶ $C(u, v, w)$ or C_{uvw} is the integral of the product of the three Legendre polynomials P_u, P_v, P_w . This vanishes unless u, v, w form a triangle of even perimeter. The following are all the values needed for $s, p, d,$ and f electrons: $C_{000} = 2, C_{011} = \frac{2}{3}, C_{022} = \frac{2}{5}, C_{033} = \frac{2}{7}, C_{011} = 2/(2l+1); C_{112} = \frac{4}{15}, C_{123} = \frac{8}{35}, C_{134} = \frac{8}{63};$

$C_{1, l, l+1} = (2l+2)/(2l+1)(2l+3);$
 $C_{222} = \frac{4}{35}, C_{224} = \frac{4}{35}, C_{233} = \frac{8}{105}, C_{235} = \frac{2}{2} \frac{2}{31}, C_{334} = \frac{4}{7}, C_{336} = \frac{2}{3} \frac{2}{3} \frac{2}{3} \frac{2}{3}.$

so that the coefficients in this sum are independent of the closed shells which the configuration may contain and are those ordinarily calculated in getting at the electrostatic energies by Slater's method.

Now the equations (6), (7) will in general give a different set of radial factors for each state of a configuration. To solve these separately for each state would be not only extremely laborious but quite without significance, since in general actual atomic states are not even approximately represented by single orbital functions of the type we have used, but *are* approximately represented by linear combinations of such functions belonging to the same configuration. Hence it would seem desirable to find one particular set of R 's to use as a basis for a first-order perturbation calculation of the energies of a given configuration by a process such as that applied by Hartree and Black⁷ to the Hartree functions for oxygen. The best set to use is probably that giving the lowest average value for the energies of the states of the configuration.⁸ This is achieved by averaging (1) over the allowed states before minimizing. The only change in the equations is that (7) now contains values A_{av}^k and B_{av}^k obtained by averaging A^k and B^k . This averaging is easily done from the known formulas for the electrostatic energies in LS coupling. By the diagonal-sum rule and the fact that the trace of the matrix of spin-orbit interaction vanishes⁹ for any configuration, this process gives that set of radial factors for which the center of gravity of the configuration is a minimum for any coupling, just as if the spin-orbit interaction had been included in the original Hamiltonian. If the R 's are obtained in this way, expression (5) is seen to give the center of gravity of the configuration. The intervals

⁷ Hartree and Black, Proc. Roy. Soc. A139, 311 (1933).

⁸ This averaging over the states of the configuration is exactly what Hartree accomplishes when he averages his fields over all directions if we consider that in Hartree's case the Pauli principle does not enter to exclude states in which two electrons have the same quantum numbers. The exclusion principle in the Fock case makes the averaging somewhat more complicated in principle.

Instead of minimizing the average energy of the states of the configuration (which amounts to minimizing the trace of the energy matrix), one could as easily minimize the average energy of the terms occurring, or the average energy of the levels occurring, but these averages seem to have less real significance and are not independent of coupling.

⁹ See, e.g., Condon and Shortley, reference 4, p. 259.

between terms must be obtained by a separate calculation of F 's and G 's with these functions.

As an example, let us consider the configuration $1s^2 2s^2 2p^2$ of C I, N II, or O III. Here, since the value $l=2$ for the incomplete shell occurs only once, all off-diagonal λ 's may be set equal to zero. We shall not write the equations referring to the $1s$ and $2s$ shells, since they are obtained immediately from (6). The dependence of the energy on the two electrons of the incomplete p shell is given by the familiar formulas

$${}^1S = F^0(np, np) + 1\frac{1}{2}\frac{5}{5}F^2(np, np) \quad (1),$$

$${}^1D = F^0(np, np) + 1\frac{1}{2}\frac{5}{5}F^2(np, np) \quad (5), \quad (8)$$

$${}^3P = F^0(np, np) - 5\frac{1}{2}\frac{5}{5}F^2(np, np) \quad (9).$$

These terms have the degeneracies indicated. Averaged over the 15 states, $A_{av}^0(np, np) = 1$, $A_{av}^2(np, np) = -\frac{2}{25}$. Inserting these values in (7) we find as the equation referring to the $2p$ shell

$$\begin{aligned} & [2O^p + 4T^0(1s, 1s) + 4T^0(2s, 2s)]R(2p) \\ & - \frac{2}{3}T^1(2p, 1s)R(1s) - \frac{2}{3}T^1(2p, 2s)R(2s) \\ & + [2T^0(2p, 2p) - \frac{4}{25}T^2(2p, 2p)]R(2p) \\ & = \lambda^2 p R(2p). \quad (9) \end{aligned}$$

This gives a set of equations of precisely the form to be solved by the method of Fock and Petraschen.²

We might note here the values of the sum over $K \subset Q$ of (7) obtained in averaging the energies of various other configurations:¹⁰

$$\begin{aligned} np^3 & [6T^0(np, np) - 1\frac{1}{2}\frac{5}{5}T^2(np, np)]R(np) \\ np^4 & : [12T^0(np, np) - 2\frac{1}{2}\frac{5}{5}T^2(np, np)]R(np) \\ nd^2 & : [2T^0(nd, nd) - \frac{4}{63}T^2(nd, nd) \\ & \quad - \frac{4}{63}T^4(nd, nd)]R(nd) \\ npn'p & \text{ (in equation referring to } np \text{ shell):} \\ T^0(n'p, n'p)R(np) & - \frac{1}{6}T^0(np, n'p)R(n'p) \\ & \quad - \frac{1}{15}T^2(np, n'p)R(n'p) \\ p^3s & \text{ (in equation referring to } p \text{ shell):} \\ [6T^0(p, p) - 1\frac{1}{2}\frac{5}{5}T^2(p, p) & = 3T^0(s, s)]R(p) \\ & \quad - \frac{1}{2}T^1(p, s)R(s) \end{aligned}$$

(in equation referring to s shell):

$$3T^0(p, p)R(s) - \frac{1}{2}T^1(s, p)R(p).$$

We have not yet a very good approximation to the $1s^2 2s^2 2p^2$, $2p^3$, or $2p^4$ configurations of C,

¹⁰ The formulas for p^3s on p. 199 of Condon and Shortley contain an error: The coefficients of G_1 in 3S , 5S should be $+1$, -3 ; cf. Van Vleck, J. Chem. Phys. 2, 20 (1934). Further, to get the whole of the contribution of the p shell, the constant term $-10F_2$ needs to be added to the energies given for p^4 on this same page.

N, or O. These configurations have a spread which is not negligible compared to their distances from other configurations, and the intervals between terms do not have the ratios which are necessarily given by a first-order theory which uses a single set of radial functions. Further, a glance at an energy-level plot such as that on p. 218 of Condon and Shortley leads one to fear that a direct calculation of configuration interaction would be hopelessly slow in converging. The question is whether one can find a better procedure.

One thing we are sure of—in all the low lying configurations the Landé intervals are relatively very small—hence except very near the series limits these atoms must be accurately in Russell-Saunders coupling and S and L must be accurate quantum numbers. This suggests that one seek separately for the best set of radial factors for each separate term, e.g., for 1S of p^2 . In order to keep the equations to the Fock type we restrict ourselves to the configuration $1s^2 2s^2 2p^2$ but now look for the best radial factors with which to form the eigenfunctions of a term of 1S symmetry. These factors are obtained by minimizing the energy of this term, taking from (8) the coefficients of F 's and G 's referring to incomplete shells. The equations for the radial factors are obtained by inserting these coefficients in the sum over $K \subset Q$ in (7). Thus for $1s^2 2s^2 2p^2$ the equations referring to the $1s$ and $2s$ shells are given by (6) and are the same for each term; the equations referring to the $2p$ shell are the same as (9) except for the coefficient of $T^2(2p, 2p)$ $R(2p)$, which is seen from (8) to be $2/5$ for 1S , $2/5$ for 1D , and $-1/5$ for 3P .

This procedure will give a different set of radial factors for each term. Using the radial factors obtained in consideration of a given term, we see that expression (5) gives directly the first-order energy of the term without further calculation.

In this process the intervals between terms are no longer constrained to definite ratios, and it is to be expected that if it were carried through it would give intervals close to those actually observed. This process would certainly give better functions than those obtained from any equations which contemplate using the same radial factors for each term.

This type of calculation could be made the basis of a higher order perturbation calculation in which functions for a particular type of term, say 1S , were calculated for a number of configurations of an atom, together with first-order energies and the nondiagonal matrix components connecting the 1S 's of different configurations, and these inserted in a secular equation to get improved energies. This process would be expected to converge much faster than the one usually contemplated since all fields have been determined to be as good as possible for 1S , without compromise with terms of other type. So long as the magnetic interactions are neglected, no terms of type other than 1S would need to be taken into consideration.

Note added to proof, Nov. 9, 1936. Professor C. W. Ufford has just called to the writer's attention, unfortunately after the type for this note has been set, a paper by D. R. Hartree and W. Hartree¹¹ which appeared during the summer. The authors of this paper not only recognize the possibility of writing Fock equations for individual terms but have calculated the Fock functions for Be $1s^2 2s 2p$, 1P and 3P . In this case, as expected, the calculated singlet-triplet separation is much closer to the observed value than is that calculated by evaluating the G integral with Hartree functions. The fact that the $2s$ radial function for 1P contains *two* nodes instead of the expected *one* raises the question of the exact meaning which may be assigned to the total quantum number when using this scheme for excited states, and indicates that its direct relation to the number of nodes is not possible.

In a still more recent paper¹² Hartree and Hartree calculate the Fock functions for Cl^- . In checking the coefficients of F 's and G 's for complete shells given on page 48 of this paper, we have found an error in Table I(b): the value of B_{220} should be 10 in place of 20; in general $B_{ll0} = 2(2l+1)$. It may be noted that our Eqs. (6), (7), above, constitute an extension, to the case where incomplete shells are involved, of that given by Hartree and Hartree for a configuration involving purely closed shells.

¹¹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A154**, 588 (1936).

¹² D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A156**, 45 (1936).