DERIVATION OF 1/Z EXPANSION OF HARTREE-FOCK EQUATIONS

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ABSTRACT.—A simple method of deriving the 1/Z expansion of the Hartree-Fock equation by using the properties of determinants and the orthonormalities of spin and space is described. The method consists of an elementary derivation of the energy expression and subsequent variation of it using Lagrange multipliers. It can also be used to derive the regular (restricted or unrestricted) Hartree-Fock equations.

In recent years, the usefulness of the 1/Z expansion perturbation method for calculating atomic wave functions and energy states, and for predicting atomic properties has been widely explored (Hirschfelder, Brown and Epstein, 1964; Dalgarno, 1962). The method involves use of the perturbation parameter, which is the inverse nuclear charge Z. It has the advantage that all members of an iso-electronic sequence may be treated simultaneously. Furthermore, it also provides a convenient basis for comparison with similar expansions corresponding to the non-relativistic many-electron Schrödinger equation. The zeroth-order equations of this method are satisfied by hydrogenic wave-functions and energies; the first-order perturbed equations using this method have been solved for a number of systems either variationally (Dalgarno, 1960) or in terms of infinite sums of Laguerre functions) Linderberg, 1961; Sharma and Coulson, 1962). For predicting many atomic properties, the calculations are very simple using this method, convergence is rapid and results are comparable in accuracy with those of the Hartree-Fock approximation. The 1/Z expansion method may be developed further to yield results superior in accuracy to those of the Hartree-Fock approximation. It is well known that the Hartree-Fock approximation has played an important role in the development of theories of atomic structure. Its quantitative application leads to a set of coupled integro differential equations, specific to the particular atomic system under consideration, which can be solved only by lengthy numerical techniques. If we apply the 1/Z expansion method to the Hartree-Fock equations, it leads to sets of uncoupled ordinary differential equations, specific to the particular electron shell under consideration, which can be solved exactly in analytical form. For this reason, many calculations have been done by this method in the last few years (e.g. Cohen and Dalgarno, 1961, 1963a, 1963b, 1964, 1965a, 1965b, 1967; Schwartz, 1962; Coulson and Hibbert, 1967; Stewart, 1964; Sharma, 1962). However, no detailed derivation of the 1/Z expansion of the Hartree-Fock equations has been shown in any of those papers or in any standard quantum mechanics textbooks except perhaps for a very brief description of the standard procedure of the derivation. The purpose of the present note is to show that a simple method of derivation can be obtained by using the properties of determinants, spin orthonormality and space orthonormality.

Notation

In order to illustrate the procedure, let us consider the case of the restricted Hartree-Fock wave function for a $1s^2 2p 2^2p$ state of excited lithium atom by using the following notations:

$\overset{+}{S}(i)$: 1s orbital with α spin for the ith electron.

$\bar{S}(i)$: 1s orbital with β spin for the ith electron.

$\overset{+}{P}_o(i)$: $2p_o$ orbital with α spin for the ith electron.

$\bar{P}_o(i)$: $2p_o$ orbital with β spin for the ith electron.

$U(r_i)$: the radial part of the 1s orbital for the ith electron.

$Y_o^o(\theta_i,\phi_i)$: the angular part of 1s orbital for the ith electron which is equal to $\frac{1}{\sqrt{4\pi}}$

$V(r_i)$: the radial part of the $2p_o$ orbital for the ith electron.

$Y_1^o(\theta_i\phi_i)$: the angular part of the $2p_o$ orbital for ith electron which is equal to $\sqrt{\frac{3}{4\pi}}\cos\theta_i$.

so the total wavefunction for the 1s orbital with α spin for the ith electron can be expressed as $\overset{+}{S} = Y_o^o(\theta_i,\phi_i)U(r_i)\alpha_i = \frac{1}{\sqrt{4\pi}}U(r_i)\alpha_i$, and the space part of the wavefunction is $S(i) = \frac{1}{\sqrt{4\pi}}U(r_i)$. Similarly, $\overset{+}{P}_o(i) = Y_1^o(\theta_i,\alpha_i)V(r_i)\alpha_i = \sqrt{\frac{3}{4\pi}}\cos\theta_i V(r_i)\alpha_i$ and $P_o(i) = \sqrt{\frac{3}{4\pi}}\cos\theta_i V(r_i)$. The inverse interelectron distance, $\frac{1}{r_{ij}}$, can be expressed as follows (Eyring, Walter and Kimble, 1947):

$$\frac{1}{r_{ij}} = \sum_{k=o}^{\infty}\sum_{m=-k}^{+k}\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}Y_k^m(\theta_i,\phi_i)Y_k^{m*}(\theta_j,\phi_m).$$

We define the following integrals:

$$|S(1)P_o(1)) = \int_{v_1}\frac{1}{r_{12}}U(r_1)V(r_1)Y_o^o(\theta_1,\phi_1)Y_1^o(\theta_1,\phi_1)\mathrm{Sin}\theta_1 d\theta_1 d\phi_1 r_1^2 dr_1$$

$$= \sum_{k=0}^{\infty} \sum_{m=-k}^{+k} \frac{4\pi}{2k+1} \int_0^{\infty} \frac{r_<^k}{r_>^{k+1}} U(r_1)V(r_1)r_1^2 dr_1$$

$$\times \int_0^{\pi}\int_0^{2\pi} \frac{1}{\sqrt{4\pi}} Y_0^0(\theta_1,\phi_1)Y_k^m(\theta_1,\phi_1)\text{Sin }\theta_1 d\theta_1 d\phi_1 Y_k^{m*}(\theta_2,\phi_2).$$

The above reduces to:

$$|S(1)P_0(1)) = \frac{\sqrt{4\pi}}{3} Y_1^0(\theta_2,\phi_2)\{ \frac{1}{r_2^2} \int_0^{r_2} r_1^3 U(r_1)V(r_1)dr_1 + r_2\int_{r_2}^{\infty} U(r_1)V(r_1)dr_1 \}$$

since the spherical harmonics form an orthonormal set, i.e.

$$\int_0^{2\pi}\int_0^{\pi} Y_k^{m*}(\theta,\phi)Y_{k'}^{m'}(\theta,\phi)\text{Sin}\theta\, d\theta\, d\phi = \delta_{k,k'}\delta_{m,m'}$$

$$(S(2)S(2)|S(1)P_0(1)) = \langle S(2)S(2) \frac{1}{r_{12}}|S(1)P_0(1)\rangle$$

$$= \frac{1}{\sqrt{4\pi}}\cdot\frac{1}{\sqrt{4\pi}}\cdot\frac{\sqrt{4\pi}}{3}\int_0^{\infty} U(r_2)\{\frac{1}{r_2^2}\int_0^{r_2} r_1^3 U(r_1)V(r_1)dr_1 + r_2\int_{r_2}^{\infty} U(r_1)V(r_1)dr_1\} r_2^2 dr_2$$

$$\times\int_0^{\pi}\int_0^{2\pi} Y_1^0(\theta_2,\phi_2)\text{Sin}\theta_2 d\theta_2 d\phi_2 = 0,$$

because $\int_0^{\pi}\int_0^{2\pi} Y_1^0(\theta_2,\phi_2)\text{Sin}\theta_2 d\theta_2 d\phi_2 = 0$ therefore the integral vanishes.

In general,

$$|SP_0) = \frac{\sqrt{4\pi}}{3} Y_1^0(\theta,\phi)\{\frac{1}{r^2}\int_0^r x^3 U(x)V(x)dx + r\int_r^{\infty} U(x)V(x)dx\},$$

$(SS|SP_0) = 0$ and $(P_0P_0|SP_0) = 0$ due to the orthonormal property of the spherical harmonics.

However, $(SP_0|SP_0) = \frac{1}{\sqrt{4\pi}}\frac{\sqrt{4\pi}}{3}\int_0^{\pi}\int_0^{2\pi} Y_1^0(\theta,\phi)Y_1^0(\theta,\phi)\text{Sin}\theta\, d\theta\, d\phi \int_0^{\infty} U(r)V(r)$

$$\times\{\frac{1}{r^2}\int_0^r x^3 U(x)V(x)dx + r\int_0^{\infty} U(x)V(x)dx\} r^2 dr,$$

or $(SP_\circ|SP_\circ) = \frac{1}{3}\int_\circ^\infty U(r)V(r)\{\frac{1}{r^2}\int_\circ^r x^3U(x)V(x)dx + r\int_r^\infty U(x)V(x)dx\}r^2dr,$

because $\int_\circ^\pi\int_\circ^{2\pi} Y_1^\circ(\theta,\phi)Y_1^\circ(\theta,\phi)\text{Sin}\theta d\theta d\phi = 1$

Similarly, we define

$$|S(1)S(1)) = \int_{V_1}\frac{1}{r_{12}}U^2(r_1)Y_\circ^\circ(\theta_1,\phi_1)Y_\circ^\circ(\theta_1,\phi_1)\text{Sin}\theta_1 d\theta_1 d\phi_1 r_1^2 dr_1$$

$$= \sum_{k=o}^{\infty}\sum_{m=-k}^{+k}\frac{4\pi}{2k+1}\int_\circ^\infty \frac{r_<^k}{r_>^{k+1}}U^2(r_1)r_1^2dr_1\int_\circ^\pi\int_\circ^{2\pi}Y_\circ^\circ(\theta_1,\phi_1)Y_\circ^\circ(\theta_1,\phi_1)Y_k^m(\theta_1,\phi_1)$$

$$\times\ \text{Sin}\theta_1 d\theta_1 d\phi_1 Y_k^{m*}(\theta_2\phi_2) = \frac{1}{r_2}\int_\circ^{r_2}U^2(r_1)r_1^2dr_1 + \int_{r_2}^\infty U^2(r_1)r_1dr_1$$

So, $(SS|P_\circ P_\circ) = (P_\circ P_\circ|SS) = \int_\circ^\pi\int_\circ^{2\pi}Y_1^\circ(\theta,\phi)Y_1^\circ(\theta,\phi)\text{Sin}\theta d\theta d\phi\int_\circ^\infty v^2(r)$

$$\times[\frac{1}{r}\int_\circ U^2(x)x^2dx + \int_r^\infty v^2(x)xdx]r^2dr$$

In general, $(P_\circ P_\circ|SS) = \int_\circ^\infty v^2(r)[\frac{1}{r}\int_\circ^r U^2(x)x^2dx + \int_r^\infty U^2(x)xdx]r^2dr,$

and $(SS|SS) = \int_\circ^\infty U^2(r)[\frac{1}{r}\int_\circ^r U^2(x)x^2dx + \int_r^\infty U^2(x)xdx]r^2dr.$

<u>1/Z Expansion of the Angular and Radial Hartree-Fock Equations</u>

We use a unit of length equal to 1/Z A.U., a unit of energy equal to Z^2 A.U. and the notations of the preceding section. The Hamiltonian of this system can be written as

$$\hat{H} = \sum_i^3 \hat{h}(i) + \frac{1}{Z}\sum_{i<j} g(i,j)$$

where $\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \frac{1}{r_i}$ and

$$\sum_{i<j} g(i,j) = \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}$$

In order to obtain the total energy of this atomic state, we have to evaluate the diagonal matrix elements of the Hamiltonian of this system over the restricted Hartree-Fock wavefunctions. Let us first consider the matrix elements of $\sum_i^3 \hat{h}(i)$. Let $\hat{\mathcal{P}}_i$ be the permutation operator and $\mathcal{P}_i$ be the number of permutation.

Then, after multiplying by inverse permutations and their corresponding signs to eliminate the normalization factor (Eyring, Walter and Kimble, 1947) we have,

$$\langle|\overset{+}{S}\bar{S}\overset{+}{P}_o|\sum_i^3 \hat{h}(i)|\overset{+}{S}\bar{S}\overset{+}{P}_o|\rangle = \frac{1}{\sqrt{3!}}\frac{1}{\sqrt{3!}} \sum_i (-1)^{\mathcal{P}_i} \hat{\mathcal{P}}_i' \overset{+}{S}(1)\bar{S}(2)\overset{+}{P}_o(3) \sum_i \hat{h}(i) \begin{vmatrix} \overset{+}{S}(1) & \bar{S}(1) & \overset{+}{P}_o(1) \\ \overset{+}{S}(2) & \bar{S}(2) & \overset{+}{P}_o(2) \\ \overset{+}{S}(3) & \bar{S}(3) & \overset{+}{P}_o(3) \end{vmatrix}$$

$$= \langle\overset{+}{S}(1)|\hat{h}(1)|\bar{S}(1)\rangle + \langle\bar{S}(2)|\hat{h}(2)|\bar{S}(2)\rangle + \langle\overset{+}{P}_o(3)|\hat{h}(3)|\overset{+}{P}_o(3)\rangle$$

$$= 2\langle S|\hat{h}|S\rangle + \langle P_o|\hat{h}|P_o\rangle;$$

where $\langle\overset{+}{S}(i)|\bar{S}(i)\rangle = \langle\bar{S}(i)|\overset{+}{S}(i)\rangle = 0$ and $\langle\overset{+}{S}(i)|\hat{h}(i)|\bar{S}(i)\rangle = \langle\bar{S}(i)|\hat{h}(i)|\overset{+}{S}(i)\rangle = 0$, because of spin orthogonality; $\langle\overset{+}{P}_o(i)|\overset{+}{S}(i)\rangle = \langle\overset{+}{S}(i)|\overset{+}{P}(i)\rangle = 0$ and $\langle\overset{+}{P}_o(i)|\hat{h}(i)|\overset{+}{S}(i)\rangle = \langle\overset{+}{S}(i)|\hat{h}(i)|\overset{+}{P}_o(i)\rangle = 0$, because of space orthogonality; $\langle\overset{+}{P}_o(i)|\hat{h}(i)|\bar{S}(i)\rangle = \langle\bar{S}(i)|\hat{h}(i)|\overset{+}{P}_o(i)\rangle = 0$, because of spin and space orthogonality;

$\langle \overset{+}{S}(i)|\hat{h}(i)|\overset{+}{S}(i)\rangle = \langle S(i)|\hat{h}(i)|S(i)\rangle\langle\alpha(i)|\alpha(i)\rangle =$ $\langle S(i)|\hat{h}(i)|S(i)\rangle \times 1 = \langle S|\hat{h}|S\rangle$ and similarly $\langle \overset{+}{P}_o(i)|\hat{h}(i)|\overset{+}{P}_o(i)\rangle =$ $\langle P_o|\hat{h}|P_o\rangle$. For matrix elements of $1/Z \sum_{i<j} g_{ij}$, we can use similar arguments to get the following results.

$$\langle|\overset{+}{S}\bar{S}\overset{+}{P}_o|\frac{1}{Z}\sum_{i<j} g_{ij}|\overset{+}{S}\bar{S}\overset{+}{P}_o|\rangle = \frac{1}{Z}\int \overset{+}{S}(1)\bar{S}(2)\overset{+}{P}_o(3)g_{12} \begin{vmatrix} \overset{+}{S}(1) & \bar{S}(1) & \overset{+}{P}_o(1) \\ \overset{+}{S}(2) & \bar{S}(2) & \overset{+}{P}_o(2) \\ \overset{+}{S}(3) & \bar{S}(3) & \overset{+}{S}(3) \end{vmatrix} dV_{123} +$$

$$\frac{1}{Z}\int S^{+}(1)S(2)P_o(3)g_{13} \begin{vmatrix} \overset{+}{S}(1) & \bar{S}(1) & \overset{+}{P}_o(1) \\ \overset{+}{S}(2) & \bar{S}(2) & \overset{+}{P}_o(2) \\ \overset{+}{S}(3) & \bar{S}(3) & \overset{+}{P}_o(3) \end{vmatrix} dV_{123}$$

$$+ \frac{1}{Z}\int \overset{+}{S}(1)\bar{S}(2)\overset{+}{P}_o(3)g_{23} \begin{vmatrix} \overset{+}{S}(1) & \bar{S}(1) & \overset{+}{P}_o(1) \\ \overset{+}{S}(2) & \bar{S}(2) & \overset{+}{P}_o(2) \\ \overset{+}{S}(3) & \bar{S}(3) & \overset{+}{P}_o(3) \end{vmatrix} dV_{123}$$

The above equation can be simplified by multiplying the third orbital ($\overset{+}{P}_o$) into the third row in the first term, the second orbital ($\bar{S}$) into the second row in the second term and the first orbital ($\overset{+}{S}$) into the first row in the third term, as shown by the arrows. After using the orthonormality argument, we have the following results:

$$\langle|\overset{+}{S}\bar{S}\overset{+}{P}_o|\frac{1}{Z}\sum_{k<j} g_{ij}|\overset{+}{S}\bar{S}\bar{P}_o|\rangle = \frac{1}{Z}\{\int \overset{+}{S}(1)\bar{S}(2)g_{12}\begin{vmatrix} \overset{+}{S}(1) & \bar{S}(1) \\ \overset{+}{S}(2) & \bar{S}(2) \end{vmatrix} dV_{12}$$

$$+ \int \overset{+}{S}(1)\overset{+}{P}_o(3)g_{13}\begin{vmatrix} \overset{+}{S}(1) & \overset{+}{P}_o(1) \\ \overset{+}{S}(3) & \overset{+}{P}_o(3) \end{vmatrix} dV_{13}$$

$$+ \int \bar{S}(2)\overset{+}{P}_o(3)g_{23}\begin{vmatrix} \bar{S}(2) & \overset{+}{P}_o(2) \\ \bar{S}(3) & \overset{+}{P}_o(3) \end{vmatrix} dV_{23}\}$$

$$= \frac{1}{Z}(SS+SS) + \frac{1}{Z}(SS|P_oP_o) - \frac{1}{Z}(SP_o|P_oS) + \frac{1}{Z}(SS|P_oP_o)$$

$$= \frac{1}{Z}\ (SS|SS) + 2(SS|P_oP_o) - (SP_o|P_oS)\}$$

So, the total energy of ($1s^2 2p\ 2^2P$) is

$$E(1s^2 2p, 2^2P) = 2(S|\hat{h}|S) + (P_o|\hat{h}|P_o) + \frac{1}{Z}(SS|SS) + \frac{2}{Z}(SS|P_oP_o) - \frac{1}{Z}(SP_o|P_oS) \tag{1}$$

The orthonormality conditions are

$$\int S^2 dV = 1, \quad \int P_o^{\,2} dV = 1 \text{ and } \quad \int SP_o dV = 0.$$

Applying the variational principle to obtain the Hartree-Fock equations, we use a star * to label the quantities being varied in Eq. (1). We have then

$$E = 2(S^*|\hat{h}|S) + (P_o^*|\hat{h}|P_o) + \frac{1}{Z}(S^*S|S^*S) + \frac{2}{Z}(S^*S|P_o^*P) - \frac{1}{Z}(S^*P_o|P_o^*S) \tag{2}$$

and we note that

$\delta\{E-2\lambda_s(S^*|S)-\lambda_p(P_o^*|P_o)-\lambda_{sp}(S^*|P_o)-\lambda_{ps}(P_o^*|S)\} = 0$ is the same

as $\delta\{E-2\lambda_s(S^*|S)-\lambda_p(P_o^*|P)-\lambda^*_{sp}(S|P_o^*)-\lambda^*_{ps}(P_o|S^*)\} = 0$, since λ_{sp}

is real, $\lambda_{sp} = \lambda^*_{ps}$ where λ's are Lagrange multipliers and $(S|S)$, $(P_o|P_o)$ and $(S|P_o)$ are the constraints.

Carrying out the variation with respect to δs^*, δP_o^*, (and to δs, αP_o separately); we have,

$$2(\delta S^*|\hat{h}|S) + (\delta P_o^*|\hat{h}|P_o) + \frac{2}{Z}(\delta S^*S|S^*S) + \frac{2}{Z}(\delta S^*S|P_o^*P_o)$$

$$+ \frac{2}{Z}(S^*S|\delta P_o^*P_o) - \frac{1}{Z}(\delta S^*P_o|P_o^*S) - \frac{1}{Z}(S^*P_o|\delta P_o^*S)$$

$$- \frac{2}{Z}\lambda_s(\delta S^*|S) - \lambda_p(\delta P_o^*|P_o) - \lambda_{sp}(\delta S^*|P_o) - \lambda_{ps}(\delta P_o^*|S) = 0$$

where $\lambda_{sp} = \lambda_{ps}$. Equating to zero the coefficients of δs^* and δP_o^*, we obtain the Hartree-Fock equations:

$$\hat{h}S + \frac{1}{Z}S|SS) + \frac{1}{Z}S|P_oP_o) - \frac{1}{2Z}P_o|P_oS) = \lambda_s S + \frac{1}{2}\lambda_{sp}P_o \quad (3)$$

$$\hat{h}P_o + \frac{2}{Z}P_o|SS) - \frac{1}{Z}S|SP_o) = \lambda_p P_o + \lambda_{ps}S \quad (4)$$

Since S and P_o are orthonormal, we do not need to introduce the Lagrangian multipliers λ_{sp} and λ_{ps}; therefore, we set $\lambda_{sp} = \lambda_{ps} = 0$, and Eqs. (3) and (4) become

$$\hat{h}S + \frac{1}{Z}S|SS) + \frac{1}{Z}S|P_oP_o) - \frac{1}{2Z}P_o|P_oS) = \lambda_s S \quad (5)$$

$$\hat{h}P_o + \frac{2}{Z}P_o|SS) - \frac{1}{Z}S|SP_o) = \lambda_p P_o \quad (6)$$

These equations depend on the parameter Z^{-1} as well as the λ's. S and P_o can be obtained as functions of that parameter by solving these equations. The present procedure also can be used to derive regular Hartree-Fock (restricted or unrestricted) equations. The derivation of the regular Hartree-Fock equations can be considered as a special case of the present method. All procedures are the same, except that we omit the 1/Z factor in the equations.

ACKNOWLEDGMENT

The author would like to acknowledge helpful discussions with Dr. A. Golebiewski of the Department of Theoretical Chemistry, Jagiellonian University, Poland and Professor Y. N. Chiu of the Catholic University of America. He also wishes to thank Dr. Dennis Sardella of Boston College for reading the manuscript.

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Manuscript received August 10, 1969