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ON THE DERIVATION OF THE HARTREE–FOCK EQUATIONS

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A simple general derivation of the Hartree—Fock equations is given. The derivation is based on the Brillouin theorem which is proved in its most general form for a Slater determinant built up from not necessarily orthogonal spin orbitals. The Hartree—Fock equations can be obtained as a specific formulation of the Brillouin theorem for the case of orthogonal spin orbitals.

As the possibility of finding alternative derivations of the Hartree—Fock equations has been the subject of recent discussion in the literature [1, 2], it seems to be of interest to present the following simple and general derivation based on the Brillouin theorem. This theorem is treated not as a consequence of the Hartree—Fock equations but is first proved to be a necessary condition which should be satisfied for the Slater determinant wave function with the lowest energy value. It is then shown that the theorem is also a necessary and sufficient condition for the stationariness of the energy expectation value and that the Hartree—Fock equations can be obtained as consequences of the Brillouin theorem. This second part of the treatment has some similarities to those given by DAHL et al. [2] and LEFEBVRE [3] but is more general (and also more general than the usual derivation [4]) because no restriction is put on the variations of the one-electron orbitals. It is usual either to consider specified variations [1—3] or to introduce Lagrangian multipliers [2, 4] in order to ensure that the one-electron orbitals remain orthogonal even after variation. Since, however, any Slater determinant wave function can also be built up from orthonormalized spin orbitals, the conservation of the orthogonality of the spin orbitals puts no physically meaningful restriction on the variations of the wave function; accordingly, as will be seen, there is no need for such a condition.

The Brillouin theorem for the Slater determinant with the lowest energy value

The Brillouin theorem states that: The matrix element of the n-electron Hamiltonian vanishes between the n-electron single Slater determinant wave function giving the lowest expectation value for the energy (the "best" Slater

determinant) and any single Slater determinant wave function which can be obtained from the former by replacing one filled spin orbital with an arbitrary unfilled spin orbital orthogonal to the filled orbitals (i.e. there is no mixing between these wave functions).

If the interchanged spin orbitals have different spins the theorem is trivial, owing to the orthogonality of the spin functions; and if they have the same spins, an indirect proof can be given.

Let us assume that the "best" Slater determinant is

$$\Psi_0 = \mathcal{A}\,[\varphi_1(1)\varphi_2(2)\ldots\varphi_i(i)\ldots\varphi_n(n)], \tag{1}$$

i.e. for a given n-electron Hamiltonian $\hat{H}$ the lowest expectation value $\bar{H} = H_{00}$ belongs to Ψ_0. We denote by Ψ_1 the wave function which can be obtained from Ψ_0 by replacing the spin orbital φ_i with a spin orbital ψ_i:

$$\Psi_1 = \mathcal{A}\,[\varphi_1(1)\varphi_2(2)\ldots\psi_i(i)\ldots\varphi_n(n)]. \tag{2}$$

$\langle\varphi_k \mid \psi_i\rangle = 0$, hence $\langle\Psi_0 \mid \Psi_1\rangle = 0$. There is no need to assume that the spin orbitals φ_k are mutually orthogonal; the appropriate normalization coefficients should be included in the antisymmetrizing operator $\mathcal{A}$.

Let us assume that the theorem is not valid, i.e. that Ψ_0 is the "best" Slater determinant but $H_{01} \neq 0$.

First we form a linear combination

$$\Psi = c_1\Psi_0 + c_2\Psi_1\,, \tag{3}$$

and determine the coefficients in such a way as to obtain a minimum energy for the wave function Ψ. The lowest root of the secular equation

$$\begin{vmatrix} H_{00}-E & H_{01} \\ H_{01}^* & H_{11}-E \end{vmatrix} = 0 \tag{4}$$

is

$$E_2 = H_{00} + \frac{1}{2}(H_{00} - H_{11})\left[\sqrt{1 - \frac{4|H_{01}|^2}{(H_{00}-H_{11})^2}} - 1\right]. \tag{5}$$

(The notation $H_{ij} = \langle\Psi_i \mid \hat{H} \mid \Psi_j\rangle$ is used).

According to our assumption $H_{00} < H_{11}$, therefore if $H_{01} \neq 0$, then E_2 will be smaller than H_{00}. It is easy to see, however, that the wave function Ψ is the sum of two determinants differing only in one row and thus can be written as a single determinant:

$$\Psi = \mathcal{A}[\varphi_1(1)\varphi_2(2)\ldots(c_1\varphi_i + c_2\psi_i)(i)\ldots\varphi_n(n)]. \tag{6}$$

(The appropriate normalization coefficients should be included in the c_i-s and $\mathcal{A}$.)

The wave function Ψ can thus be written as a single Slater determinant. Its energy E_2 is lower than H_{00} and consequently Ψ_0 cannot be the "best" Slater determinant. This contradicts the original premise, thus the theorem is proved. (If, however, $H_{01} = 0$, the lowest root of the secular equation is $E = H_{00}$.)

The Brillouin theorem for a Slater determinant with a stationary energy value

To vary the wave function $\Psi_0 = \mathcal{A}[\varphi_1(1)\varphi_2(2) \ldots \varphi_n(n)]$ normalized to 1 the spin orbitals must be varied. There is no need to regard the spin orbitals as orthonormalized, accordingly there is no need to require that this property be conserved during the variation. It should be noted that the normalization of the determinant wave function can change during the most general variation.

Let

$$\delta\varphi_k = \eta \sum_{\lambda=1}^{\infty} c_{k\lambda}\, \varphi_\lambda\, \delta(\chi_k, \chi_\lambda), \qquad (7)$$

$$(\chi = \alpha \text{ or } \beta)$$

where η is an arbitrary complex quantity tending to zero. This variation is the most general one, because one can construct a complete system of functions from the filled orbitals having spin χ_k and from arbitrary unfilled orbitals of the same spin which are orthogonal to the filled orbitals. The only requirement is that the function represented by the sum should be finite and regular. Evidently an arbitrary number of $c_{k\lambda}$-s can be equal to zero, which permits the realization of specific variations. The wave function obtained after the variation is a determinant for which every element is the sum of two terms $[(\varphi_k + \delta\varphi_k)(i)]$, and it can therefore be written as a sum of 2^n determinants. The majority of these, however, are proportional to the square or to higher powers of η and are therefore negligible as compared with terms of the first order in η ("independence of the variations"). Accordingly,

$$\begin{aligned} \delta\Psi &= \sum_{k}^{n} \mathcal{A}[\varphi_1(1)\,\varphi_2(2) \ldots \delta\varphi_k(k) \ldots \varphi_n(n)] = \\ &= \eta \sum_{k=1}^{n} \sum_{\lambda=1}^{\infty} c_{k\lambda}\, \delta(\chi_k, \chi_\lambda)\, \mathcal{A}[\varphi_1(1)\,\varphi_2(2) \ldots \varphi_\lambda(k) \ldots \varphi_n(n)]. \end{aligned} \qquad (8)$$

Summing over λ separately up to n and from $n + 1$:

$$\delta\Psi = \eta \left\{ \sum_{k=1}^{n} c_{kk}\, \Psi_0 + \sum_{k=1}^{n} \sum_{\lambda=n+1}^{\infty} c_{k\lambda}\, \delta(\chi_k, \chi_\lambda)\, \mathcal{A}[\varphi_1(1)\,\varphi_2(2) \ldots \varphi_\lambda(k) \ldots \varphi_n(n)] \right\}. \qquad (9)$$

In the sum corresponding to the values $\lambda \leqslant n$ we have taken into account that if $\lambda \neq k$ the determinants have two equal rows.

The norm of the wave function after variation is

$$\langle \Psi_0 + \delta\Psi \mid \Psi_0 + \delta\Psi \rangle = 1 + \langle \delta\Psi \mid \Psi_0 \rangle + \langle \Psi_0 \mid \delta\Psi \rangle + \langle \delta\Psi \mid \delta\Psi \rangle. \quad (10)$$

The last term is proportional to η^2 and can be omitted. It is easy to see that

$$\begin{aligned} \langle \delta\Psi | \Psi_0 \rangle &= \eta^* \sum_{k=1}^{n} c_{kk}^* , \\ \langle \Psi_0 | \delta\Psi \rangle &= \eta \sum_{k=1}^{n} c_{kk} \end{aligned} \quad (11)$$

because Ψ_0 is orthogonal to all terms of the second sum in the expression for $\delta\Psi$. ($\langle \varphi_k \mid \varphi_\lambda \rangle = 0$, if $k \leqslant n$, $\lambda > n$.)

Thus we obtain

$$\langle \Psi_0 + \delta\Psi | \Psi_0 + \delta\Psi \rangle = 1 + \eta^* \sum_{k=1}^{n} c_{kk}^* + \eta \sum_{k=1}^{n} c_{kk}. \quad (12)$$

The expectation value of the Hamiltonian after variation is

$$\begin{aligned} \bar{H} + \delta\bar{H} = H_{00} + \delta\bar{H} = \frac{\langle \Psi_0 + \delta\Psi | \hat{H} | \Psi_0 + \delta\Psi \rangle}{\langle \Psi_0 + \delta\Psi | \Psi_0 + \delta\Psi \rangle} = \\ = \frac{1}{1 + \eta^* \sum_{k=1}^{n} c_{kk}^* + \eta \sum_{k=1}^{n} c_{kk}} \left\{ \left\langle \Psi_0 \left(1 + \eta \sum_{k=1}^{n} c_{kk} \right) \middle| \hat{H} \middle| \Psi_0 \left(1 + \eta \sum_{k=1}^{n} c_{kk} \right) \right\rangle + \right. \\ + \eta^* \sum_{k=1}^{n} \sum_{\lambda=n+1}^{\infty} c_{k\lambda}^* \, \delta(\chi_k, \chi_\lambda) \langle \mathcal{A}[\varphi_1(1)\varphi_2(2) \ldots \varphi_\lambda(k) \ldots \varphi_n(n)] \mid \hat{H} \mid \Psi_0 \rangle + \\ \left. + \eta \sum_{k=1}^{n} \sum_{\lambda=n+1}^{\infty} c_{k\lambda} \, \delta(\chi_k, \chi_\lambda) \langle \Psi_0 | \hat{H} | \mathcal{A}[\varphi_1(1)\varphi_2(2) \ldots \varphi_\lambda(k) \ldots \varphi_n(n)] \rangle \right\}. \end{aligned} \quad (13)$$

We have again dropped the terms proportional to η^2. After a further term containing η^2 has been omitted and the division by the denominator standing at the beginning of the expression has been carried out, the first matrix element gives just $H_{00} = \langle \Psi_0 \mid \hat{H} \mid \Psi_0 \rangle$, and we obtain

$$\begin{aligned} \delta\bar{H} = \frac{\eta^* \sum_{k=1}^{n} \sum_{\lambda=n+1}^{\infty} c_{k\lambda}^* \, \delta(\chi_k, \chi_\lambda) \langle \mathcal{A}[\varphi_1(1)\varphi_2(2) \ldots \varphi_\lambda(k) \ldots \varphi_n(n)] \mid \hat{H} \mid \Psi_0 \rangle}{1 + \eta^* \sum_{k=1}^{n} c_{kk}^* + \eta \sum_{k=1}^{n} c_{kk}} + \\ + \text{complex conjugate.} \end{aligned} \quad (14)$$

It follows that for arbitrary variations $\delta\bar{\bar{H}} = 0$ if, and only if, the Brillouin theorem is satisfied, i.e. the Slater determinant Ψ_0 has a stationary value of $\bar{H}$ ($\delta\bar{H} = 0$) if, and only if, the matrix element of the Hamiltonian is zero between Ψ_0 and any Slater determinant which can be obtained from Ψ_0 by replacing one filled orbital by an unfilled orbital which is orthogonal to the filled orbitals. LEFEBVRE [3] earlier gave a derivation of the Brillouin theorem for the case of a Slater determinant with a stationary energy value, using a similar but not identical method.

It follows from the comparison of the above two theorems that if there exists a Slater determinant for which the energy reaches its exact lower limit (for the set of wave functions which can be written with a single Slater determinant), this Slater determinant will have a stationary energy value too. This is usually assumed in all approaches based on the variation principle, although it is questionable whether it may be regarded as evident *a priori* for all types of trial wave functions.

The Hartree—Fock equations as consequences of the Brillouin theorem

Using an appropriate orthogonalization procedure one can always arrange that the wave function Ψ_0 considered in the discussion of the Brillouin theorem be given as a Slater determinant built up from orthonormalized spin orbitals. In this case we can obtain the Hartree—Fock equations expressing the Brillouin theorem in terms of one-electron orbitals.

According to the Brillouin theorem

$$\langle \Psi_0 | \hat{H} | \Psi_1 \rangle = 0 , \tag{15}$$

where

$$\hat{H} = \sum_{l}^{n} H^N(l) + \sum_{l<k}^{n} \frac{1}{r_{lk}} . \tag{16}$$

H^N is the one-electron part of the Hamiltonian.

Ψ_0 and Ψ_1 differ in one spin orbital, as above: instead of φ_l in Ψ_0, there is ψ_r in Ψ_1. Since the Brillouin theorem is trivial if $\chi_l \neq \chi_r$, we assume $\chi_l = \chi_r$. All spin orbitals concerned are orthonormalized, and so, using the known formulae [4], Eq. (15) can be rewritten in terms of the integrals over the spatial parts of the orbitals:*

$$\int \varphi_l^*(1)\, H^N(1)\, \psi_r(1)\, dv_1 + \sum_{i \neq l}^{n} \left[\iint \varphi_l^*(1)\, \varphi_l^*(2) \frac{1}{r_{12}} \varphi_i(1)\, \psi_r(2)\, dv_1\, dv_2 - \right.$$
$$\left. - \delta(\chi_i, \chi_l) \iint \varphi_l^*(1)\, \varphi_l^*(2) \frac{1}{r_{12}} \psi_r(1)\, \varphi_i(2)\, dv_1\, dv_2 \right] = 0 . \tag{17}$$

* Here and further on φ and ψ denote only those parts of the orbitals which depend on the spatial coordinates.

Taking the complex conjugate of this equation, using the hermiticity of the operator H^N in the first integral and interchanging the notations of the variables of integration in the second one, we obtain

$$\int \psi_r^*(1)\, H^N(1)\, \varphi_l(1)\, dv_1 + \sum_{i\neq l}^{n}\left[\iint \psi_r^*(1)\, \varphi_l^*(2)\, \frac{1}{r_{12}}\, \varphi_i(2)\, \varphi_l(1)\, dv_1\, dv_2 - \right.$$
$$\left. - \delta(\chi_i, \chi_l) \iint \psi_r^*(1)\, \varphi_l^*(2)\, \frac{1}{r_{12}}\, \varphi_i(1)\, \varphi_l(2)\, dv_1\, dv_2 \right] = 0\,. \tag{18}$$

Taking the integration over r_1 separately and contracting:

$$\int \psi_r^*(1) \left\{ H^N(1)\, \varphi_l(1) + \sum_{i\neq l}^{n}\left[\left(\int |\varphi_i(2)|^2 \frac{1}{r_{12}}\, dv_2 \right) \varphi_l(1) - \right.\right.$$
$$\left.\left. - \delta(\chi_i, \chi_l) \left(\int \varphi_l^*(2)\, \varphi_l(2) \frac{1}{r_{12}}\, dv_2 \right) \varphi_i(1) \right] \right\} dv_1 = 0\,. \tag{19}$$

This equation shows that the function of r_1 in the brackets is orthogonal to ψ_r. According to the derivation of the Brillouin theorem ψ_r may be any function orthogonal to all orbitals in Ψ_0 which have a spin χ_l. Consequently, the function in the brackets can be expressed as a linear combination of the functions occurring in Ψ_0 and having spin χ_l.

$$H^N(1)\, \varphi_l(1) + \sum_{i\neq l}^{n}\left(\int |\varphi_i(2)|^2 \frac{1}{r_{12}} dv_2 \right) \varphi_l(1) - \sum_{i\neq l}^{n} \delta(\chi_i, \chi_l) \left(\int \varphi_l^*(2)\, \varphi_l(2) \frac{1}{r_{12}} dv_2 \right) \varphi_i(1) =$$
$$= \sum_{i}^{n} \lambda_{li}\, \delta(\chi_i, \chi_l)\, \varphi_i(1)\,. \quad (l = 1, 2 \ldots n) \tag{20}$$

These are the Hartree–Fock equations [4].

The hermiticity of the λ matrix can be easily seen if one multiplies this equation by $\varphi_k^*(1)$ and the corresponding equation for φ_k by $\varphi_l^*(1)$ and then integrates both over r_1, and makes the necessary interchanges of variables of integration.

The equation can be transformed with the aid of the usual unitary transformation [4] into a pseudo-eigenvalue equation whose solutions for different orbital energies are automatically orthogonal, while solutions with equal orbital energies can be orthogonalized in such a way that the functions obtained also satisfy the Hartree–Fock equations. On the other hand the Brillouin theorem follows from the Hartree–Fock equations, so these are fully equivalent for the case of orthonormalized spin orbitals.

In the usual derivation the Lagrangian multipliers are introduced in order to ensure the orthonormality of the orbitals. As can be shown, in the

usual derivation the fact that in the case of equal orbital energies there can be solutions which are not necessarily orthogonal (even if they may be orthogonalized) is connected with a not fully consistent application of the Lagrangian multipliers.

Except for the first theorem, the present derivation can be applied without any essential change for the case of doubly filled orbitals; one has only to take into account that the spatial parts of the orbitals and their variations and the terms in formula (14) describing the variation of the energy are equal in pairs.

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О ВЫВОДЕ УРАВНЕНИЙ ХАРТРИ–ФОКА

И. МАЙЕР

Резюме

Приводится простой и общий вывод уравнений Хартри–Фока. Вывод основан на теореме Бриллюэна, которая доказывается в наиболее общем виде для детерминантной волновой функции, построенной из не обязательно ортогональных спин-орбиталей. Система уравнений Хартри–Фока может быть получена как специальная формулировка теоремы Бриллюэна для случая ортогональных спин-орбиталей.