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Note on an Approximation Treatment for Many-Electron Systems

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A perturbation theory is developed for treating a system of n electrons in which the Hartree-Fock solution appears as the zero-order approximation. It is shown by this development that the first order correction for the energy and the charge density of the system is zero. The expression for the second-order correction for the energy greatly simplifies because of the special property of the zero-order solution. It is pointed out that the development of the higher approximation involves only calculations based on a definite one-body problem.

THE Hartree-Fock method[1] for treating a system of n electrons in a given external field consists in making the approximation of assigning to the system a wave function of the determinantal form

$$\Phi^\circ=\frac{1}{(n!)^{\frac{1}{2}}}\begin{vmatrix}\varphi_1(q_1) & \varphi_1(q_2) & \cdots & \varphi_1(q_n)\\ \varphi_2(q_1) & \cdot & \cdots & \cdot\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ \varphi_n(q_1) & \cdot & \cdots & \varphi_n(q_n)\end{vmatrix}, \qquad (1)$$

where the variables q_i represent space and spin coordinates, and the n functions $\varphi_r(q)$ are a set of orthogonal normalized solutions of the equation

$$i\hbar(\partial/\partial t)\varphi_r(q)=(H_0+B-A)\varphi_r(q). \qquad (2)$$

In (2) H_0 is the Hamiltonian for an electron in the external field, and the matrix elements of B and A in the q-representation are given by[2]

$$(q|B|q')=\int\int(qq''|V|q'q''')dq''dq'''(q'''|\rho|q''), \qquad (3)$$

$$(q|A|q')=\int\int(qq''|V|q'''q')dq''dq'''(q'''|\rho|q''), \qquad (4)$$

where the matrix of ρ is defined by

$$(q|\rho|q')=\sum_{r=1}^{n}\varphi_r(q)\varphi_r^*(q'), \qquad (5)$$

and V is the interaction energy for a pair of electrons.

As follows from the definition (5) the density matrix ρ is Hermitean and obeys the equation $\rho^2=\rho$; (5) together with (2) give the equation of motion for ρ

$$i\hbar\dot{\rho}=(H_0+B-A)\rho-\rho(H_0+B-A). \qquad (6)$$

As Dirac has emphasized, all probabilities can be expressed by means of this density matrix ρ;[3] in particular the charge density at q is given by $(q|\rho|q)$.

It is supposed throughout the following that H_0 does not contain the time explicitly. We may then consider solutions of (2) and (6) which belong to a stationary state μ so that our equations become

$$F_\mu\varphi_r^{(\mu)}(q)\equiv(H_0+B_\mu-A_\mu)\varphi_r^{(\mu)}(q)=\lambda_r^{(\mu)}\varphi_r^{(\mu)}(q); \qquad (7)$$

$$F_\mu\rho_\mu-\rho_\mu F_\mu=0. \qquad (8)$$

It is clear that the form of the operator F_μ depends on the stationary state considered. The energy of the system is, in the present approximation, given by

$$W_\mu^\circ=D\{\rho(H_0+\tfrac{1}{2}B_\mu-\tfrac{1}{2}A_\mu)\}, \qquad (9)$$

where D denotes the diagonal sum. The corresponding wave function for a stationary state of the whole system is an eigenfunction of the operator

$$G_\mu\equiv\sum_{i=1}^{n}\{H_0^{(i)}+B_\mu^{(i)}-A_\mu^{(i)}\}=\sum_{i=1}^{n}F_\mu^{(i)}, \qquad (10)$$

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[1] V. Fock, Zeits. f. Physik **61**, 126 (1930); P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, Part III, 376 (1930).

[2] $\int\cdots dq$ is always understood to include summation over the spin coordinate.

[3] Dirac, Proc. Camb. Phil. Soc. **27**, Part II, 240 (1930).

where by $F_\mu^{(i)}$ is meant the operator $H_0+B_\mu-A_\mu$ (or F_μ) operating only on functions of the coordinates of the ith electron. We have

$$G_\mu\Phi_\mu{}^\circ=\lambda_\mu\Phi_\mu{}^\circ, \tag{11}$$

in which

$$\lambda_\mu=\sum_{r=1}^{n}\lambda_r{}^{(\mu)}.$$

From (7) it follows that

$$\begin{aligned}\lambda_\mu&=\sum_{r=1}^{n}\int\varphi_r{}^{(\mu)*}\cdot F_\mu\varphi_r{}^{(\mu)}dq\\ &=\sum_{r=1}^{n}\int\int\varphi_r{}^{(\mu)*}(q)(q|F_\mu|q')\varphi_r{}^{(\mu)}(q')dqdq'\\ &=\int\int(q'|\rho_\mu|q)(q|F_\mu|q')dqdq'=D(\rho_\mu F_\mu).\end{aligned} \tag{12}$$

Comparison of (12) with (9) gives

$$\lambda_\mu=W_\mu{}^\circ+\tfrac{1}{2}D\{\rho_\mu(B_\mu-A_\mu)\}. \tag{13}$$

We may now write (11) as follows

$$\begin{aligned}H_\mu\Phi_\mu{}^\circ&\equiv[G_\mu-\tfrac{1}{2}D\{\rho_\mu(B_\mu-A_\mu)\}]\Phi_\mu{}^\circ\\ &=W_\mu{}^\circ\Phi_\mu{}^\circ.\end{aligned} \tag{14}$$

so that the operator H_μ has the eigenvalue $W_\mu{}^\circ$ and the eigenfunction $\Phi_\mu{}^\circ$.

We now wish to compare the above equation with the exact one in order to determine the degree of accuracy of the Hartree-Fock approximation. If V_{ik} denoted the interaction energy between the ith and kth electron, then the exact equation for the eigenstates of the system is

$$\mathcal{H}\Phi\equiv\left\{\sum_{i=1}^{n}H_0{}^{(i)}+\tfrac{1}{2}\sum_{i\neq k}^{n}V_{ik}\right\}\Phi=W\Phi. \tag{15}$$

It is, of course, understood that only antisymmetrical solutions of (15) are to be considered. We now compare the operators occurring in (14) and (15) and define a new operator Γ_μ as their difference,

$$\begin{aligned}\Gamma_\mu=\mathcal{H}-H_\mu=\tfrac{1}{2}\sum_{i\neq k}^{n}V_{ik}-\sum_{i=1}^{n}(B_\mu{}^{(i)}-A_\mu{}^{(i)})\\ +\tfrac{1}{2}D\{\rho_\mu(B_\mu-A_\mu)\}.\end{aligned} \tag{16}$$

It is now proposed for the succeeding development to take the Hartree-Fock-approximation as the zero-order approximation to the exact theory. The deviation, Γ_μ, of the Hartree-Fock operator H_μ from the exact operator $\mathcal{H}$ is here regarded as a small perturbation; and it is evident that the form of this perturbation term depends on the stationary state considered. We develop the exact eigenfunction Φ_μ, which is supposed to lie near the Hartree-Fock solution $\Phi_\mu{}^\circ$, and the exact eigenvalue W_μ, which is supposed to lie near the corresponding $W_\mu{}^\circ$, in the following series

$$\Phi_\mu=\Phi_\mu{}^\circ+\Phi_\mu{}^{(1)}+\Phi_\mu{}^{(2)}+\cdots, \tag{17}$$

$$W_\mu=W_\mu{}^\circ+W_\mu{}^{(1)}+W_\mu{}^{(2)}+\cdots. \tag{18}$$

If these expansions are introduced into the exact equation $(H_\mu+\Gamma_\mu)\Phi_\mu=W_\mu\Phi_\mu$ it is found on collecting terms of the same magnitude in the usual way that

$$H_\mu\Phi_\mu{}^\circ=W_\mu{}^\circ\Phi_\mu{}^\circ; \tag{19}$$

$$\{H_\mu-W_\mu{}^\circ\}\Phi_\mu{}^{(1)}=\{W_\mu{}^{(1)}-\Gamma_\mu\}\Phi_\mu{}^\circ; \tag{20}$$

$$\{H_\mu-W_\mu{}^\circ\}\Phi_\mu{}^{(2)}=W_\mu{}^{(2)}\Phi_\mu{}^\circ\{W_\mu{}^{(1)}-\Gamma_\mu\}\Phi_\mu{}^{(1)}; \tag{21}$$

Eq. (19) is of course fulfilled from the definition (14) of the zero-order approximation; (20) and (21) are the equations determining the first and second order corrections, respectively.

Let us consider the complete set of eigenfunctions $\Phi_{\mu\nu}{}^\circ$ of the Hartree-Fock operator H_μ associated with a definite zero-order state μ; we have

$$H_\mu\Phi_{\mu\nu}{}^\circ=W_{\mu\nu}{}^\circ\Phi_{\mu\nu}{}^\circ, \tag{22}$$

where $W_{\mu\nu}{}^\circ$ are the corresponding eigenvalues, and where we choose ν so that $\Phi_{\mu 0}{}^\circ=\Phi_\mu{}^\circ$. The functions $\Phi_\mu{}^{(1)}$, $\Phi_\mu{}^{(2)}$, $\cdots$ may be developed in terms of the complete set of functions $\Phi_{\mu\nu}{}^\circ$; that is,

$$\Phi_\mu{}^{(1)}=\sum_\nu a_{\mu\nu}{}^{(1)}\Phi_{\mu\nu}{}^\circ; \tag{23}$$

$$\varphi_\mu{}^{(2)}=\sum_\nu a_{\mu\nu}{}^{(2)}\Phi_{\mu\nu}{}^\circ; \tag{24}$$

$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\;.$$

Substitution of (23) into (20) and application of (22) gives

$$\sum_\nu A_{\mu\nu}{}^{(1)}(W_{\mu\nu}{}^\circ-W_\mu{}^\circ)\Phi_{\mu\nu}{}^\circ=\{W_\mu{}^{(1)}-\Gamma_\mu\}\Phi_\mu{}^\circ. \tag{25}$$

If the right side of Eq. (25) is expanded in terms of the functions $\Phi_{\mu\nu}^{\circ}$ and corresponding coefficients equated, one gets at once

$$a_{\mu\nu}^{(1)}(W_{\mu\nu}^{\circ}-W_{\mu}^{\circ}) =\int\cdots\int\Phi_{\mu\nu}^{\circ *}\{W_{\mu}^{(1)}-\Gamma_{\mu}\}\Phi_{\mu}^{\circ}dq. \quad (26)$$

Let us for simplicity suppose that $W_{\mu\nu}^{\circ}\neq W_{\mu}$ for $\nu\neq 0$; the alterations in the procedure which arise in the presence of degeneracies are of the usual kind and will not be considered here. From (26) for $\nu=0$ we have

$$W_{\mu}^{(1)}=\int\cdots\int\Phi_{\mu}^{\circ *}\Gamma_{\mu}\Phi_{\mu}^{\circ}dq; \quad (27)$$

and for $\nu\neq 0$

$$a_{\mu\nu}^{(1)}=\frac{\int\cdots\int\Phi_{\mu\nu}^{\circ *}\Gamma_{\mu}\Phi_{\mu}^{\circ}dq}{W_{\mu}^{\circ}-W_{\mu\nu}^{\circ}}. \quad (28)$$

The normalization condition for Φ_{μ} gives $a_{\mu 0}^{(1)}=0$. The second order correction may be carried through in a similar way by the introduction of (24) into (21); it is readily found that the second order correction in the energy is

$$W_{\mu}^{(2)}=\sum_{\nu\neq 0}\frac{\int\cdots\int\Phi_{\mu}^{\circ *}\Gamma_{\mu}\Phi_{\mu\nu}^{\circ}dq\cdot\int\cdots\int\Phi_{\mu\nu}^{\circ *}\Gamma_{\mu}\Phi_{\mu}^{\circ}dq}{W_{\mu}^{\circ}-W_{\mu\nu}^{\circ}}. \quad (29)$$

The complete set of antisymmetric eigenfunctions in (22) may be expressed in terms of the complete set of eigenfunctions of the one-electron operator F_{μ}. In addition to the n functions $\varphi_r^{(\mu)}$, which enter into the determinant Φ_{μ}°, we have an infinite set of eigenfunctions $\psi_{\rho}^{(\mu)}(\rho=1, 2, \cdots)$ of F_{μ} with the associated eigenvalues κ_{ρ}. We now get all the functions $\Phi_{\mu\nu}^{\circ}$ from

$$\Phi_{\mu}^{\circ}=\frac{1}{(n!)^{\frac{1}{2}}}\begin{vmatrix}\varphi_1^{(\mu)}(q_1) & \varphi_1^{(\mu)}(q_2) & \cdots & \varphi_1^{(\mu)}(q_n)\\ \varphi_2^{(\mu)}(q_1) & \cdot & \cdots & \cdot\\ \cdot & & & \cdot\\ \cdot & & & \cdot\\ \varphi_n^{(\mu)}(q_1) & \cdot & \cdots & \varphi_n^{(\mu)}(q_n)\end{vmatrix}, \quad (30)$$

by replacing one or more of the functions $\varphi^{(\mu)}$ by functions $\psi^{(\mu)}$. We denote by $\Phi^{\circ}_{(\mu)r,\, s\cdots;\, \rho,\, \sigma,\, \ldots}$ that $\Phi_{\mu\nu}^{\circ}$ which is obtained by replacing $\varphi_r^{(\mu)}$, $\varphi_s^{(\mu)}\cdots$ by $\psi_{\rho}^{(\mu)}$, $\psi_{\sigma}^{(\mu)}$, $\cdots$ respectively; the indices $r, s\cdots$ may take on independently all the values $1\cdots n$, and $\rho, \sigma\cdots$ take on all values.

It will be understood in the following that all quantities refer to a given stationary state, and the suffix μ will be dropped. From (27) and (16) we get for the first order correction in the energy

$$\begin{aligned}W^{(1)}=&(1/(n!2))\sum_{i\neq k}^{n}\int\cdots\int(q_iq_k|V|q_i'q_k')\sum_{PP'}\delta_P P\varphi_1^*(q_1)\varphi_2^*(q_2)\cdots\varphi_n^*(q_n)\delta_{P'}P'\varphi_1(q_1)\varphi_2(q_2)\\ &\qquad\cdots\varphi_i(q_i')\cdots\varphi_k(q_k')\cdots\varphi_n(q_n)dq_1dq_2\cdots dq_ndq_i'dq_k'\\ &-(1/n!)\sum_{i=1}^{n}\int\cdots\int(q_i|B-A|q_i')\sum_{PP'}\delta_P P\varphi_1^*(q_1)\cdots\varphi_n^*(q_n)\delta_{P'}P'\varphi_1(q_1)\cdots\varphi_i(q_i')\\ &\qquad\cdots\varphi_n(q_n)dq_1\cdots dq_ndq_i'+\tfrac{1}{2}D\{\rho(B-A)\}, \qquad (31)\\ =&\,\mathrm{I}+\mathrm{II}+\tfrac{1}{2}D\{\rho(B-A)\},\end{aligned}$$

where P denotes a permutation of the arguments of the functions φ^*, δ_P is $+1$ or -1 according as P is an even or odd permutation, and $\sum_P$ includes $n!$ possible permutations; similarly P' denotes all permutations of the arguments of the functions φ. To calculate the first of the integrals in (31) we consider that term in $\sum_{PP'}$ which comes from $P=P'$, a definite permutation; a typical term, for the given P, in $\sum_{i\neq k}$ is

$$\frac{1}{n!2}\int\int\int\int (q_iq_k|V|q_i'q_k')\varphi_r^*(q_i)\varphi_s^*(q_k)\varphi_r(q_i')\varphi_s(q_k')dq_idq_kdq_i'dq_k'$$

$$=\frac{1}{n!2}\int\int\int\int (qq'|V|q''q''')\varphi_r^*(q)\varphi_s^*(q')\varphi_r(q'')\varphi_s(q''')dqdq'dq''dq''', \quad (32)$$

where r, s are the respective places to which P has taken q_i, q_k. If now the summation over i, k is carried out, we get

$$\frac{1}{n!2}\sum_{r\neq s}^{n}\int\int\int\int (qq'|V|q''q''')\varphi_r^*(q)\varphi_s^*(q')\varphi_r(q'')\varphi_s(q''')dqdq'dq''dq'''.$$

Clearly, every $P=P'$ gives this same result so that $\sum_{P=P'}$ gives a factor $n!$ and the contribution to I is, using (5) and (3),

$$\tfrac{1}{2}\int\int (q''|\rho|q)(q|B|q'')dqdq''$$

$$-\sum_{i=1}^{n}\int\int\int\int (qq'|V|q''q''')\varphi_i^*(q)\varphi_i^*(q')\varphi_i(q'')\varphi_i(q''')dqdq'dq''dq'''; \quad (33)$$

the first term in this expression, we note, is $\frac{1}{2}D(\rho B)$. We now consider the contribution to I arising from the remaining permutations $P'\neq P$. On account of the orthogonality of the functions φ_r, for a given P the only P' in $\sum_{P'}$ which contributes will differ from P merely by a transposition of the arguments of φ_r and φ_s in a typical term in $\sum_{i\neq k}$; thus the analogue of (32) is

$$-\frac{1}{n!2}\int\int\int\int (q_iq_k|V|q_i'q_k')\varphi_r^*(q_i)\varphi_s^*(q_k)\varphi_r(q_k')\varphi_s(q_i')dq_idq_kdq_i'dq_k';$$

the negative sign enters since $\delta_P=-\delta_{P'}$. As before $\sum_{i\neq k}$ and $\sum_P$ may be immediately carried out to give

$$-\tfrac{1}{2}D(\rho A)+\tfrac{1}{2}\sum_{i=1}^{n}\int\int\int\int (qq'|V|q''q''')\varphi_i^*(q)\varphi_i^*(q')\varphi_i(q'')\varphi_i(q''')dqdq'dq''dq'''. \quad (34)$$

Thus from (33) and (34)

$$\mathrm{I}=\tfrac{1}{2}D\{\rho(B-A)\}. \quad (35)$$

In a similar way we find that $\mathrm{II}=-D\{\rho(B-A)\}$; and we have finally from (31) that

$$W^{(1)}=0. \quad (36)$$

Thus, the perturbation method shows that the theory of the self-consistent field including exchange is accurate in the determination of energy to the second approximation.

We shall now consider the matrix elements entering into the determination of the first order correction (28) in the eigenfunction and the second order correction (29) in the energy. It is evident that those integrals, $\int\cdots\int\Phi_\nu^\circ\Gamma\Phi^\circ dq$ in which Φ_ν° has more than two of the functions φ_r replaced by functions ψ_ρ will vanish identically because of the orthogonality of the functions φ and ψ. The only integrals, therefore, which remain are of the form

$$\int\cdots\int\Phi^\circ{}_{r;\ \rho}\Gamma\Phi^\circ dq \quad (37) \qquad \text{and} \qquad \int\cdots\int\Phi^\circ{}_{rs;\ \rho\sigma}\Gamma\Phi^\circ dq. \quad (38)$$

A straight forward calculation of the integrals of the type (37) shows that it is a special property of the Hartree-Fock theory that all these integrals vanish; however, we get a nonvanishing contribution from the integrals (38) of the form

$$\int\cdots\int\Phi^\circ{}_{rs;\,\rho\sigma}\Gamma\Phi^\circ dq=\int\int\int\int\psi_\rho{}^*(q)\psi_\sigma{}^*(q')(qq'|V|q''q''')\cdot\{\varphi_r(q'')\varphi_s(q''')-\varphi_r(q''')\varphi_s(q'')\}dqdq'dq''dq'''. \quad (39)$$

Eq. (29) now reduces to

$$W^{(2)}=\sum_{rs;\,\rho\sigma}\frac{|\int\int\int\int\psi_\rho{}^*(q)\psi_\sigma{}^*(q')(qq'|V|q''q''')\{\varphi_r(q'')\varphi_s(q''')-\varphi_r(q''')\varphi_s(q'')\}dqdq'dq''dq'''|^2}{\lambda_r+\lambda_s-\kappa_\rho-\kappa_\sigma} \quad (40)$$

where we have used the relations

$$W^\circ=\sum_{i=1}^{n}\lambda_i-\tfrac{1}{2}D\{\rho(B-A)\}\,; \qquad \text{and} \qquad W^\circ{}_{rs;\,\rho\sigma}=\kappa_\rho+\kappa_\sigma+\sum_{i\neq r,\,s}\lambda_i-\tfrac{1}{2}D\{\rho(B-A)\}.$$

As we now see from (40) and (28), to carry the procedure to this higher approximation it is only necessary to find the solutions of the equation $F_\mu\psi=\kappa\psi$; that is, to solve a one-body problem.

The wave functions including the first order correction are in a similar way reduced to

$$\Phi^\circ+\Phi^{(1)}=\Phi^\circ+\sum_{rs;\,\rho\sigma}a^{(1)}{}_{rs;\,\rho\sigma}\Phi^\circ{}_{rs;\,\rho\sigma} \quad (41)$$

as $a^{(1)}{}_{rs;\,\rho\sigma}$ are the only non-zero coefficients from (28). The charge distribution corresponding to (41) is

$$\rho(q)=n\int\cdots\int\left|\Phi^\circ(q,\,q_2,\,q_3\cdots q_r)+\sum_{rs;\,\rho\sigma}a^{(1)}{}_{rs;\,\rho\sigma}\Phi^\circ{}_{rs;\,\rho\sigma}(q,\,q_2,\,q_3\cdots q_n)\right|^2dq_2dq_3\cdots dq_n. \quad (42)$$

It is readily seen that the cross terms in (42) which give the first order correction to $\rho(q)$ all vanish so that the Hartree-Fock electric density as given by the diagonal elements of (5) is accurate to the second order.