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# STABILITY CONDITIONS AND NUCLEAR ROTATIONS IN THE HARTREE-FOCK THEORY

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**Abstract:** An expression for a general Slater determinant is written in the notation of second quantization. This expression has just the right number of arbitrary coefficients, so no subsidiary conditions are required, and the expression for a particular determinant is unique. This notation is used to study two problems. Firstly, a condition for a particular solution of the Hartree-Fock equations to minimize the expectation value of the Hamiltonian is derived. This condition is equivalent to the condition for stability of collective modes in the random phase approximation. Secondly, the determinant which minimizes the expectation value of the Hamiltonian while giving a particular value to the expectation value of a component of angular momentum is found. In this way, an expression for the moment of inertia of an axially symmetric system is derived within the framework of the Hartree-Fock theory. The expression for a determinant is generalized to include the type of wave functions used in the theory of superconductivity.

## 1. Introduction

There is a considerable amount of arbitrariness in the representation of a Slater determinant, since any set of linear combinations of the wave functions which make up the determinant gives rise to the same determinant. On the other hand, although the density matrix uniquely determines the determinant, it must satisfy a subsidiary condition in order to be the density matrix of a determinantal wave function [1]). It is convenient to use a representation in which the numbers of coefficients is equal to the number of degrees of freedom of an $N$-particle determinant, and such a representation is developed in sect. 2 of this paper.

The representation is used to calculate the conditions that a determinant must satisfy in order to minimize the expectation value of the Hamiltonian. The condition that the first derivatives with respect to the coefficients should be zero gives the Hartree-Fock self-consistent field equations, but the condition that the second derivatives should be non-negative gives an additional condition which must be satisfied. This new condition is the same as the condition for collective modes to be stable in the random phase approximation.

The representation is also used to find a determinant which gives a particular value for the expectation value of the angular momentum, and which also minimizes the Hamiltonian. In the first approximation, the additional energy is

proportional to the square of the angular momentum, for a nonspherical system, and the constant of proportionality gives an expression for the moment of inertia.

The representation can be generalized in an obvious way to give the type of wave functions which are used in the theory of superconductivity as a first approximation. This generalization is shown to be equivalent to the usual definitions of such wave functions in terms of quasi-particle operators, but no applications are worked out.

## 2. Representation of a Slater Determinant

We wish to represent a general Slater determinant $|\Phi\rangle$ for a system of $N$ particles by use of creation and annihilation operators in a particular representation. The operator $a_i^+$ creates a particle with wave function $\varphi_i$ and the operator $a_i$ annihilates a particle with wave function $\varphi_i$. We denote by $|\Phi_0\rangle$ the configuration in which the first $N$-levels are occupied, so that

$$|\Phi_0\rangle = (\prod_{i=1}^{N} a_i^\dagger)|0\rangle, \tag{1}$$

where $|0\rangle$ denotes the vacuum, in which no particles are present. Written in this form, $|\Phi_0\rangle$ is normalized to unity.

*Theorem.* Any $N$-particle Slater determinant $|\Phi\rangle$ which is not orthogonal to $|\Phi_0\rangle$ can be written in the form

$$\begin{aligned} |\Phi\rangle &= [\prod_{i=1}^{N} \prod_{m=N+1}^{\infty} (1+C_{mi} a^\dagger{}_m a_i)]|\Phi_0\rangle \\ &= [\exp(\sum_{i=1}^{N} \sum_{m=N+1}^{\infty} C_{mi} a_m{}^\dagger a_i)]|\Phi_0\rangle, \end{aligned} \tag{2}$$

where the coefficients $C_{mi}$ are uniquely determined. Conversely, any wave function written in the form of eq. (2), with $|\Phi_0\rangle$ defined by eq. (1), is an $N$-particle Slater determinant.

This theorem is easily proved. We suppose that $|\Phi\rangle$ is a determinant of the wave functions

$$\psi_\alpha = \sum_{i=1}^{\infty} f_{\alpha i} \varphi_i, \tag{3}$$

where $\alpha$ runs from 1 to $N$. Using second quantization, we can write this Slater determinant as

$$|\Phi\rangle = [\prod_{\alpha=1}^{N} (\sum_{i=1}^{N} f_{\alpha i} a_i^\dagger + \sum_{m=N+1}^{\infty} f_{\alpha m} a_m^\dagger)]|0\rangle. \tag{4}$$

Since we have assumed that this wave function is not orthogonal to $|\Phi_0\rangle$, we can normalize it so that its scalar product with $|\Phi_0\rangle$ is unity. This gives

$$\langle\Phi_0|\Phi\rangle = \det f_{\alpha i} = 1, \tag{5}$$

where both $\alpha$ and $i$ run from 1 to $N$. We write the inverse of the $N \times N$ matrix $f_{\alpha i}$ as $F_{i\alpha}$, so that we have

$$\sum_{i=1}^{N} f_{\alpha i} F_{i\beta} = \delta_{\alpha\beta}, \quad \sum_{\alpha=1}^{N} F_{i\alpha} f_{\alpha j} = \delta_{ij}, \tag{6}$$

for $i$ and $j$ less than or equal to $N$. We can then define

$$C_{mi} = \sum_{\alpha=1}^{N} F_{i\alpha} f_{\alpha m} \tag{7}$$

for $i \leqq N$, $m > N$. We can write $N$ linear independent combinations of the wave functions $\psi_\alpha$, which are, from eqs. (3), (6) and (7),

$$\chi_i = \sum_{\alpha=1}^{N} F_{i\alpha} \psi_\alpha = \varphi_i + \sum_{m=N+1}^{\infty} C_{mi} \varphi_m. \tag{8}$$

The Slater determinant of these must be identical with $|\Phi\rangle$, so that we have

$$\begin{aligned} |\Phi\rangle &= [\prod_{i=1}^{N} (a_i^\dagger + \sum_{m=N+1}^{\infty} C_{mi} a_m^\dagger)]|0\rangle = [\prod_{i=1}^{N} (1 + \sum_{m=N+1}^{\infty} C_{mi} a_m^\dagger a_i) a_i^\dagger]|0\rangle \\ &= [\prod_{i=1}^{N} \prod_{m=N+1}^{\infty} (1 + C_{mi} a_m^\dagger a_i)]|\Phi_0\rangle. \end{aligned} \tag{9}$$

The sum over $m$ can be replaced by a product because all terms in which the same creation operator occurs more than once vanish. For the same reason, the infinite product of eq. (2) can be written as an exponential. The coefficients are uniquely determined because $C_{mi}$ is the ratio of the scalar product of $|\Phi\rangle$ with $a_m^\dagger a_i |\Phi_0\rangle$ to its scalar product with $|\Phi_0\rangle$. Thus we have proved the theorem.

The converse is obvious, since $|\Phi\rangle$ defined by eq. (2) is a determinant of the wave functions $\chi_i$ defined by eq. (8).

## 3. Stability of Solutions of the Hartree-Fock Equations

We can use our theorem to find the conditions that $|\Phi_0\rangle$ must satisfy if it minimizes the expectation value of the Hamiltonian, which we take to be

$$H = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} T_{ij} a_i^\dagger a_j + \tfrac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} V_{ij,kl} a_j^\dagger a_i^\dagger a_k a_l. \tag{10}$$

We can expand

$$E = \langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle \tag{11}$$

in powers of the $C_{mi}$, and we require that the first order term should vanish, while the second order term should be positive definite. The condition for the first order term to vanish is

$$T_{mi} + \sum_{j=1}^{N} (V_{mj,ij} - V_{mj,ji}) = 0, \tag{12}$$

and this, as is well known [2]), is satisfied if the wave functions $\varphi_i$ satisfy the Hartree-Fock self-consistent field equations. If eq. (12) is satisfied, there is no loss of generality in assuming that the representation is such that, for all $i$ and $j$, we have

$$T_{ij}+\sum_{k=1}^{N}(V_{ik,jk}-V_{ik,kj})=\varepsilon_i\delta_{ij}, \tag{13}$$

where $\varepsilon_i$ is the Hartree-Fock energy of $\varphi_i$. The expectation value of the Hamiltonian for $|\Phi\rangle_0$ is

$$E_0=\langle\Phi_0|H|\Phi_0\rangle=\sum_{i=1}^{N}T_{ii}+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(V_{ij,ij}-V_{ij,ji}). \tag{14}$$

We can substitute eq. (2) into eq. (11) to evaluate the expression up to second order in the $C_{mi}$. Making use of eqs. (13) and (14), we get

$$\langle\Phi|\Phi\rangle\approx 1+\sum_{i=1}^{N}\sum_{m=N+1}^{\infty}|C_{mi}|^2, \tag{15}$$

and

$$\begin{aligned}\langle\Phi|H|\Phi\rangle &\approx E_0\langle\Phi|\Phi\rangle+\sum_{i=1}^{N}\sum_{m=N+1}^{\infty}(\varepsilon_m-\varepsilon_i)|C_{mi}|^2\\ &+\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{m=N+1}^{\infty}\sum_{n=N+1}^{\infty}[(V_{in,mj}-V_{in,jm})C_{nj}{}^*C_{mi}+\tfrac{1}{2}(V_{ij,mn}-V_{ij,nm})C_{mi}C_{nj}\\ &+\tfrac{1}{2}(V_{mn,ij}-V_{mn,ji})C_{mi}{}^*C_{nj}{}^*].\end{aligned} \tag{16}$$

Since the normalization factor drops out, the necessary condition for $|\Phi_0\rangle$ to minimize the expectation value of the Hamiltonian is that the quadratic form on the right of eq. (16) should be non-negative definite. This means that the eigenvalues $\lambda$ of the equation

$$\begin{aligned}(\varepsilon_m-\varepsilon_i)C_{mi}+\sum_{j=1}^{N}\sum_{n=N+1}^{\infty}[(V_{jm,ni}-V_{jm,in})C_{nj}+(V_{mn,ij}-V_{mn,ji})C_{nj}{}^*]&=\lambda C_{mi},\\ (\varepsilon_m-\varepsilon_i)C_{mi}{}^*+\sum_{j=1}^{N}\sum_{n=N+1}^{\infty}[(V_{in,mj}-V_{in,jm})C_{nj}{}^*+(V_{ij,mn}-V_{ij,nm})C_{nj}]&=\lambda C_{mi}{}^*,\end{aligned} \tag{17}$$

must all be positive or zero. If the self-consistent field has some symmetry, these equations may become much simpler. For example, in the case of an infinite medium where the wave functions $\varphi_i$ may be plane waves, eq. (17) couples $C_{mi}$ to $C_{nj}$ only if the momentum difference between $\varphi_m$ and $\varphi_i$ is equal to the momentum difference between $\varphi_n$ and $\varphi_j$, and to $C_{nj}{}^*$ only if it is equal to the momentum difference between $\varphi_j$ and $\varphi_n$. In the case of a finite system, the self-consistent field may be spherically symmetric, in which case the eigenvectors of eq. (17) must be eigenvectors of angular momentum.

There is a close relation between eq. (17) and the equation for the frequencies of collective modes in the random phase approximation. Using the method of

Sawada [3]), we can derive the equation for frequencies $\omega$ of collective modes, which is

$$(\varepsilon_m-\varepsilon_i)x_{mi}+\sum_{j=1}^{N}\sum_{m=N+1}^{\infty}[(V_{jm,ni}-V_{jm,in})x_{nj}+(V_{mn,ij}-V_{mn,ji})y_{nj}] = \hbar\omega x_{ni},$$
$$(\varepsilon_m-\varepsilon_i)y_{mi}+\sum_{j=1}^{N}\sum_{m=N+1}^{\infty}[(V_{in,mj}-V_{in,jm})y_{nj}+(V_{ij,mn}-V_{ij,nm})x_{nj}] = -\hbar\omega y_{mi}. \tag{18}$$

This equation will be discussed in detail in another paper. If eq. (17) has eigenvalue zero, so has eq. (18). If one eigenvalue of eq. (17) is negative, then eq. (18) has imaginary eigenvalues. If no eigenvalue of eq. (17) is negative, then all the eigenvalues of eq. (18) are real. A collective mode with imaginary energy can build up indefinitely, and so the failure of the determinant $|\Phi_0\rangle$ to minimize the expectation value of the Hamiltonian is revealed by a unstable collective mode in the random phase approximation. This is why we refer to the "instability" of the solution of the Hartree-Fock equations. This connection between the random phase approximation and the Hartree-Fock theory is not surprising, since Goldstone and Gottfried have derived the random phase equations by using time-dependent Hartree-Fock theory [4]).

The nature of the instability which is found in a particular representation may give a clue to the nature of the best solution of the Hartree-Fock equations. For example, if quadrupole oscillations are unstable for a spherically symmetric solution, we would conjecture that the shape of the best self-consistent potential would be approximately spheroidal. This situation might occur in a model of deformed atomic nuclei. If $|\Phi_0\rangle$ is a determinant of plane waves, density fluctuations may be unstable, and the best self-consistent potential is likely to be periodic (in one, two, or all three dimensions). This possibility has been discussed by Overhauser [5]).

Unless $|\Phi_0\rangle$ is a determinant of plane waves, there are always Slater determinants which give the same expectation value of a translation-invariant Hamiltonian, because the position of the wave function does not affect the expectation value. If the self-consistent potential is not spherically symmetric, the orientation can also be changed without affecting the expectation value. An infinitesimal displacement $\mathbf{r}$ is generated by putting

$$C_{mi} = \int \varphi_m^* \mathbf{r}\cdot\nabla\varphi_i \tag{19}$$

in eq. (2), and an infinitesimal rotation about the $x$-axis is generated by putting

$$C_{mi} = \int \varphi_m^* \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} + i\sigma_x/\hbar\right)\varphi_i, \tag{20}$$

where $\sigma_x$ is the component of the spin angular momentum operator, in eq. (2). It can easily be verified that eqs. (19) and (20) give eigenvectors of eq. (17) with eigenvalue zero. The right side of eq. (19) is only zero if the self-consistent

field is translation invariant, and the right side of eq. (20) is only zero if the self-consistent field is invariant under rotations about the $x$-axis. Eq. (19) does not give an eigenvector of eq. (17) when the Hartree-Fock theory is applied to electrons in any atom, since the Hamiltonian is not translation invariant, but the nucleus of the atom provides a natural origin for the coordinate system.

## 4. The Rotational Problem

There is a natural way of calculating the moment of inertia of a system within the framework of the Hartree-Fock theory. We can try to find what determinant minimizes the expectation value of the Hamiltonian subject to the restriction that the average value of a component of the angular momentum should have a particular value. The expectation value of the Hamiltonian will generally increase as the angular momentum increases, and the rate of increase gives an estimate for the moment of inertia. This method is similar to the method proposed by Gross [6]) but Gross required the exponent on the right of eq. (2) to be a local operator, while we shall not make that requirement.

A similar method certainly gives the right answer for the translational problem. If $|\Phi_0\rangle$ is a determinant which gives zero for the expectation value of the linear momentum,

$$|\Phi\rangle = \exp[(iP/N\hbar)\sum_{i=1}^{N} x_i]|\Phi_0\rangle \tag{21}$$

is a determinant which gives $P$ for the expectation value of the $x$-component of the linear momentum. The expectation value of the energy increases by $P^2/2NM$, where $M$ is the mass of one particle, so we correctly calculate the total mass of the system to be $NM$. In this case, our method is identical with that of Gross [6]).

In the rotational problem it is not possible to get an exact answer. We suppose that the determinant $|\Phi_0\rangle$ which minimizes the expectation value of the Hamiltonian gives expectation value zero for all components of angular momentum, but that it has only axial symmetry, not spherical symmetry. The orientation of the axis of symmetry is not determined. If we require that the expectation value of the x-component of angular momentum $J_x$ have a particular very small value, the determinant which minimizes the expectation value of the Hamiltonian is very nearly equal to $|\Phi_0\rangle$ only if its axis is in the $yz$-plane. We, therefore, choose the axis of $|\Phi_0\rangle$ to be along the $z$-axis, and use eq. (2) to expand the expectation value of $J_x$. We get

$$\langle\Phi|J_x|\Phi\rangle \approx \sum_{i=1}^{N}\sum_{m=N+1}^{\infty}[(J_x)_{im}C_{mi}+C_{mi}^{*}(J_x)_{mi}], \tag{22}$$

to first order. The expectation value of the Hamiltonian is given by eq. (16),

to second order. Using the method of undetermined multipliers, we find that the equations for the coefficients $C_{mi}$ are

$$(\varepsilon_m-\varepsilon_i)C_{mi} + \sum_{i=1}^{N}\sum_{n=N+1}^{\infty}[(V_{jm,ni}-V_{jm,in})C_{nj}+(V_{mn,ij}-V_{mn,ji})C_{nj}^*] = \Omega(J_x)_{mi},$$
$$(\varepsilon_m-\varepsilon_i)C_{mi}^*+\sum_{i=1}^{N}\sum_{n=N+1}^{\infty}[(V_{in,mj}-V_{in,jm})C_{nj}^*+(V_{ij,mn}-V_{ij,mn})C_{nj}] = \Omega(J_x)_{im}, \tag{23}$$

provided that $\Omega$, and hence the expectation value of $J_x$, is sufficiently small.

If we use eqs. (16), (22) and (23) to calculate the moment of inertia, we get

$$\begin{aligned}\mathscr{I} &= (\langle\Phi|J_x|\Phi\rangle)^2/2(\langle\Phi|H|\Phi\rangle-E_0\langle\Phi|\Phi\rangle)\\ &=\sum_{i=1}^{N}\sum_{m=N+1}^{\infty}[(J_x)_{im}C_{mi}+(J_x)_{mi}C_{mi}^*]/\Omega,\end{aligned} \tag{24}$$

which is independent of $\Omega$. The solution of eq. (23) is generally quite complicated, but eq. (24) has the structure of the cranking model of Inglis [7]). If we ignore the terms which involve the interaction in eq. (23), we get immediately

$$\mathscr{I} = 2\sum_{i=1}^{N}\sum_{m=N+1}^{\infty}|(J_x)_{mi}|^2(\varepsilon_m-\varepsilon_i)^{-1}, \tag{25}$$

which is the simple cranking model formula. This follows from eq. (23) if the exchange terms in the potential are neglected, and so would be correct if the Hartree theory rather than the Hartree-Fock theory were used. In the Hartree-Fock theory corrections to the simple formula will generally be necessary. Our formula is probably rather more difficult to use than that of Gross [6]), but may yield a higher value of the moment of inertia, since the trial wave functions are less restricted.

## 5. Generalization of the Representation

We can generalize the wave function $|\Phi\rangle$, which is defined by eq. (2), in an obvious way, and get

$$\begin{aligned}|\Phi'\rangle = [\exp[\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}C_{ij}a_ia_j+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{m=N+1}^{\infty}(C_{mi}-C_{im})a_m^\dagger a_i\\ +\tfrac{1}{2}\sum_{m=N+1}^{\infty}\sum_{n=N+1}^{\infty}C_{mn}a_m^\dagger a_n^\dagger)]]|\Phi_0\rangle.\end{aligned} \tag{26}$$

This is the type of wave function which is used as a first approximation in the theory of superconductivity, and particular examples of this representation have been used by Bardeen, Cooper and Schrieffer [8]), and by Valatin [9]) in this connection. The comparison of eqs. (2) and (26) shows how this type of wave function can be regarded as a generalized Slater determinant, and why the variational method of determining the wave function is a generalization of the Hartree Fock theory [10]).

This theory is usually developed in terms of quasi-particle operators which are linear combinations of particle creation and annihilation operators. If we have a complete set of quasi-particle annihilation and creation operators $\alpha_i$, $\alpha_i^\dagger$, then there is a wave function $|\Phi'_0\rangle$ such that

$$\alpha_i|\Phi'_0\rangle = 0 \tag{27}$$

for all $i$. The determinant $|\Phi_0\rangle$ is a special case of such a wave function. It is easy to show that there is a complete set of quasiparticle annihilation operators $\beta_i$ which give zero when they operate on the wave function

$$|\Phi'\rangle = [\exp(\tfrac{1}{2}\sum_i\sum_j C_{ij}\alpha_i^\dagger\alpha_j^\dagger)]|\Phi'_0\rangle. \tag{28}$$

One such operator is proportional to

$$\alpha_i+\tfrac{1}{2}\sum_j (C_{ji}-C_{ij})\alpha_j^\dagger,$$

because of the commutation relation

$$[\alpha_i, \exp(\tfrac{1}{2}\sum_j\sum_k C_{jk}\alpha_j^\dagger\alpha_k^\dagger)] = \sum_l (C_{il}-C_{li})\alpha_l^\dagger \exp(\tfrac{1}{2}\sum_j\sum_k C_{jk}\alpha_j^\dagger\alpha_k^\dagger). \tag{29}$$

A complete set of quasi-particle annihilation operators can be chosen in this way.

The methods of this paper could be used to study whether the solution of the variational problem does minimize the expectation value of the Hamiltonian. In a particular case, it has been shown that the condition for a minimum and the condition for the stability of collective modes in the random phase approximation are identical [11]). It would also be possible to use this method to study the rotational problem in a superfluid system of fermions, although it is not obvious that the results would be different from the results obtained by Migdal [12]).

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