

Brueckner's Theory and the Method of Superposition of Configurations

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The method of superposition of configurations, which provides a general solution of the quantum-mechanical many-particle problem (for fermions), is reformulated so that equations may be compared with those used in the Brueckner theory. Important differences occur in application to finite or nonuniform systems for which the Hartree-Fock or Brueckner self-consistent orbitals are not plane waves. In such cases nonvanishing single-particle matrix elements occur which cannot be described by the Brueckner formalism based on a two-particle operator. Equations for an effective two-particle operator, equivalent to the variational equations of the method of superposition of configurations, are derived for a basis of Hartree-Fock orbitals. At the expense of making the orbital basis dependent upon the effective two-particle operator, the orbital basis can be determined by a condition which is essentially that of the Brueckner method. This condition removes a class of matrix elements which do not necessarily

vanish in the Hartree-Fock basis although they would be neglected to second order in a perturbation calculation starting from the Hartree-Fock wave function. The equations for the effective two-particle operator are formally the same in both cases but lead to different operators because of the different choice of basis. In neither case can the equations be written in terms of products of such operators, a formalism assumed in the Brueckner theory. It is shown that the Brueckner condition is not equivalent to the condition which would determine the best possible orbital basis for the form of wave function implied by the use of an effective operator dependent on two particles only. The argument of the present paper is limited to systems with a finite number of particles, since the variational principle used here is not applicable without modification to systems with an infinite number of particles.

I. INTRODUCTION

THERE is a considerable literature concerned with the solution of many-particle problems in quantum mechanics by the method of superposition of configurations.¹ This can be thought of as an extension of the Hartree-Fock self-consistent field method² but, as emphasized by Boys,³ whether or not one starts with a Hartree-Fock calculation, methods can be developed within the context of superposition of configurations which necessarily converge to an exact eigenfunction and energy eigenvalue of Schrödinger's equation.

Recently calculations on the hypothetical infinite uniform nucleus have been carried out by Brueckner and collaborators,⁴ based on a method which is formally quite different from superposition of configurations, yet also has its roots in the Hartree-Fock method. The Brueckner method has been further developed⁵ and its theoretical basis has been discussed by several writers.⁶

It has been suggested that the Brueckner method be applied to finite nuclei, and to calculations on the electronic wave functions of atoms and solids.⁷

The purpose of the present paper is to develop a version of the method of superposition of configurations in which the formal solution to the many-particle Schrödinger equation is expressed, insofar as possible, in terms of an effective two-particle reaction operator. In this development this effective operator is not and does not have to be completely defined. It exists as a collection of numbers which can be interpreted as matrix elements of a two-particle operator under certain severe restrictions—in particular that the operator depends upon a choice of basis for its matrix representation. This choice can be determined by an arbitrary auxiliary condition which may be chosen so as to simplify the equations of the method. Two such choices will be considered in this paper, the first, a condition equivalent to the Hartree-Fock equations, and the second, a condition which corresponds as closely as possible to the method of Brueckner.

The Brueckner method is primarily concerned with such an effective two-particle operator. The present paper will examine the possibility of defining such an operator, starting from a formal solution to the many-particle problem, and will discuss certain discrepancies that arise in an attempt to apply the Brueckner formalism to finite systems. The principal difficulty in finite (or nonuniform) cases is that plane-wave expansions no longer simplify the problem. Matrix elements which are identically zero because of translational

¹ L. Brillouin, *Les Champs self-consistent de Hartree et de Fock* (Hermann et Cie, Paris, 1934), No. 159 in series: *Actualités Scientifiques et Industrielles*; C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934); S. F. Boys, *Proc. Roy. Soc. (London)* **A200**, 542 (1950); P. P. Manning, *Proc. Roy. Soc. (London)* **A230**, 415, 424 (1955); P. O. Löwdin, *Phys. Rev.* **97**, 1474, 1490, 1509 (1955).

² L. Brillouin, reference 1; C. Møller and M. S. Plesset, reference 1; R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); R. McWeeny, *Proc. Roy. Soc. (London)* **A232**, 114 (1955).

³ S. F. Boys, reference 1.

⁴ Brueckner, Levinson, and Mahmoud, *Phys. Rev.* **95**, 217 (1954); K. A. Brueckner, *Phys. Rev.* **96**, 508 (1954); **97**, 1353 (1955); K. A. Brueckner and W. Wada, *Phys. Rev.* **103**, 1008 (1956).

⁵ K. A. Brueckner and C. A. Levinson, *Phys. Rev.* **97**, 1344 (1955); K. A. Brueckner, *Phys. Rev.* **100**, 36 (1955); K. M. Watson, *Phys. Rev.* **103**, 489 (1956); W. B. Riesenfeld and K. M. Watson, *Phys. Rev.* **104**, 492 (1956).

⁶ R. J. Eden and N. C. Francis, *Phys. Rev.* **97**, 1366 (1955); H. A. Bethe, *Phys. Rev.* **103**, 1353 (1956); R. J. Eden, *Phys. Rev.* **99**, 1418 (1955); *Proc. Roy. Soc. (London)* **A235**, 408 (1956); J. Goldstone, *Proc. Roy. Soc. (London)* **A239**, 267 (1957); L. S. Rodberg, *Ann. Phys.* **2**, 199 (1957).

⁷ In the present paper "the Brueckner method" will be used to denote the self-consistent procedure for finite systems summarized by Brueckner and Wada, reference 4. Secs. II and VI, and by Bethe, reference 6, Sec. III. A discussion of higher order corrections and the infinite case (where it is necessary to distinguish between the Brillouin-Wigner and Schrödinger perturbation theories) will be given in a later paper.

symmetry in the uniform infinite case no longer vanish and must be explicitly included in the theory. Matrix elements arising from one-particle transitions are of this nature. Although the auxiliary condition on the basis for representation of operators can be chosen explicitly to make a large class of one-particle matrix elements vanish, it does not seem to be possible to remove them completely from the formalism. The matrix elements of this kind which remain after application of the auxiliary condition cannot be represented as matrix elements of a two-particle operator and hence cannot be treated within the Brueckner formalism.

There are further difficulties which arise in finite systems when the determinantal function of stationary energy is degenerate or nearly degenerate. This situation is usually characterized by a configuration of unfilled shells in the independent-particle approximation. In such cases the auxiliary condition on one-particle basis functions indicated by the Hartree-Fock or Brueckner method (applied to a single determinantal function) is not in general compatible with the specialized form of such functions which is assumed in applying group theoretical techniques to simplify the problem. For example the atomic orbitals appropriate to the determinantal function of lowest energy for an unfilled atomic electron shell cannot in general be expressed as products of radial functions and single spherical harmonics, and cannot be transformed into such products without destroying the stationary property of the energy of the determinantal function. This situation has been analyzed in detail elsewhere.⁸ The general case can be treated by trivial modifications of the method of superposition of configurations without losing the considerable advantage of available group theoretical methods. It is not possible to describe the technique applicable to such cases in terms of an effective two-particle operator. Hence the Brueckner method could not be used in connection with the usual group-theoretical methods.

One of the results of the present analysis is to obtain a formalism as nearly as possible equivalent to the Brueckner method,⁷ wherever both are applicable, which is derived from the variational principle and resolves many of the apparently *ad hoc* features of the Brueckner method. Although the present paper does not make use of perturbation theory, it should be pointed out that the principal equations derived here, if used to define a calculation by successive iterations, would lead to summations over expressions which exclude only the particular "unlinked cluster" terms of perturbation theory^{5,6} that correspond to matrix elements connecting the trial state Φ_0 with itself. Other "unlinked clusters" would not be cancelled out in the truncated basis of determinantal functions considered here. These terms arise from a perturbation expansion of the total energy shift ΔE and should not be im-

portant for systems with a finite number of particles unless ΔE is comparable in magnitude to the excitation energy of the two-particle excited states closest to Φ_0 .

The variational approach of superposition of configurations cannot be used unless all integrals are finite over operators occurring in the many-particle Hamiltonian and trial one-particle wave functions. A nuclear potential with an extended "hard core" (i.e., infinite over a finite region in two-particle space) must be treated by the Brueckner method, which was designed to deal with this problem. However, in solid-state, molecular, and atomic problems the Coulomb interaction operator leads to finite integrals. Presumably both approaches are possible with suitable modifications to the Brueckner method for finite problems. Insofar as the nuclear two-particle interaction can be represented by an operator which leads to finite integrals, both approaches are again possible and should be used to complement each other.

The present paper is concerned only with finite systems for which the difference ΔE between the true energy and the Hartree-Fock energy is small. When ΔE can be neglected in comparison with the energy of doubly excited states the equations derived here are equivalent to those of the Brueckner method⁷ except for differences discussed in the text.

II. REFORMULATION OF THE METHOD OF SUPERPOSITION OF CONFIGURATIONS

The general solution to the many-particle Schrödinger equation,

$$H\Psi = E\Psi,$$

with

$$H = \sum_i T(i) + \sum_{i < j} v(i, j), \quad (1)$$

for a system of N fermions, can be expressed as

$$\Psi = \sum_{\mu} c_{\mu} \Phi_{\mu}, \quad (2)$$

where $\{\Phi_{\mu}\}$ is the set of all normalized Slater determinants

$$\Phi_{\mu} = \det \phi_{1\mu} \cdots \phi_{i\mu} \cdots \phi_{N\mu} \quad (3)$$

constructed from a complete orthonormal set of orbitals (one-particle wave functions ϕ_i). To avoid special consideration of a continuum it will be assumed that N is finite and that the set of orbitals is denumerable (there is no difficulty in extending the results to the case $N \rightarrow \infty$ and to a basis of orbitals specified by a continuous parameter). The discussion will be limited to operators (1) which have finite matrix elements between normalized determinants.

The coefficients c_{μ} in (2) are components of the eigenvector of the matrix $(\mu|H|\nu)$ corresponding to the eigenvalue E :

$$\sum_{\nu} (\mu|H|\nu) c_{\nu} = E c_{\mu}. \quad (4)$$

It can be shown⁹ that Eq. (4) is equivalent to the

⁹ See Appendix I. This is the steady-state form of the scattering matrix considered by B. Lippmann and J. Schwinger, Phys. Rev. **76**, 469 (1950); M. L. Goldberger, Phys. Rev. **84**, 929 (1951); K. M. Watson, Phys. Rev. **89**, 575 (1953).

⁸ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

homogeneous equations for an auxiliary vector $G_{\mu 0}$, where

$$G_{\mu 0} = \sum_{\nu} \frac{N_{\mu\nu} G_{\nu 0}}{E - D_{\nu}}. \quad (5)$$

Then the coefficients c_{μ} are proportional to $G_{\mu 0}/(E - D_{\mu})$. Here $N_{\mu\nu} = (\mu|H|\nu)(1 - \delta_{\mu\nu})$, a matrix with no diagonal elements; $D_{\mu} = (\mu|H|\nu)\delta_{\mu\nu}$, a purely diagonal matrix.

If the coefficient c_0 is set equal to unity (i.e., Ψ is not normalized), Eqs. (5) are equivalent to the inhomogeneous equations

$$G_{\mu 0} = N_{\mu 0} + \sum'_{\nu \neq 0} \frac{N_{\mu\nu} G_{\nu 0}}{E - D_{\nu}}, \quad (6)$$

together with the auxiliary condition

$$E = D_0 + G_{00}. \quad (6')$$

Suppose that a determinant Φ_0 has been constructed from the first N of an orthonormal set of orbitals. Indices $i, j, k, \dots \leq N$ will be used for this set, and indices $a, b, c, \dots > N$ will be used for other orbitals from a complete orthonormal set. Then the complete orthonormal set of determinants Φ_{μ} can be classified as

$$\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}, \Phi_{ijk}^{abc}, \dots, \quad (7)$$

where the lower indices $i < j < k < \dots \leq N$ denote orbitals occupied in Φ_0 which are replaced by orbitals $N < a < b < c < \dots$ in determinant $\Phi_{\mu} = \Phi_{ijk\dots}^{abc\dots}$.

Consistently with this notation, $\sum_{ijk\dots}$ will be used to denote a summation over all n -tuples of indices with $i < j < k < \dots \leq N$. Correspondingly $\sum_{abc\dots}$ denotes summation over $N < a < b < c < \dots$.

For a Hamiltonian of the form (1), there are no matrix elements between Φ_0 and any determinant in which more than two orbitals have been changed.

Hence, if Φ_0 is in some sense an approximation to the true wave function Ψ , it will be a better approximation to diagonalize H over the set $\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}$, which includes all determinants having matrix elements with Φ_0 . Equations (6) for this problem are:

$$(0|G|0) = \sum_i \sum_a \frac{(0|H|i^a)(i^a|G|0)}{E - D_i^a} + \sum_{ij} \sum_{ab} \frac{(0|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}^{ab}}, \quad (8)$$

$$(i^{a'}|G|0) = (i^{a'}|H|0) + \sum_i \sum_a \frac{(i^{a'}|H|i^a)(i^a|G|0)}{E - D_i^a} + \sum_{ij} \sum_{ab} \frac{(i^{a'}|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}^{ab}}, \quad (8')$$

$$(i'j^{a'b'}|G|0) = (i'j^{a'b'}|H|0) + \sum_i \sum_a \frac{(i'j^{a'b'}|H|i^a)(i^a|G|0)}{E - D_i^a} + \sum_{ij} \sum_{ab} \frac{(i'j^{a'b'}|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}^{ab}}. \quad (8'')$$

The diagonal matrix elements of H are to be omitted in all summations.

The auxiliary condition (6') becomes

$$E = (0|H|0) + (0|G|0). \quad (9)$$

If determinants $\Phi_{i'j^{a'b'c}}$ were added to the basis set, there would be an additional set of equations (8''') for matrix elements

$$(i'j^{a'b'c'}|G|0),$$

and additional terms involving such matrix elements in Eqs. (8') and (8''). Since all matrix elements of the form

$$(0|H|ijk^{abc})$$

vanish for a Hamiltonian of the form (1), there would be no additional terms in Eq. (8). The new determinants affect the energy only indirectly through the matrix elements $(i^a|G|0)$ and $(ij^{ab}|G|0)$. These equations become equivalent to the original Schrödinger equation when the orbitals form a complete set and all determinants $\Phi_{ijk\dots}^{abc\dots}$ are included.

It is possible to interpret the sets of numbers

$$(i^a|G|0), (ij^{ab}|G|0), (ijk^{abc}|G|0), \text{ etc.},$$

as matrix elements of effective operators G_1, G_2, G_3 , etc., which are symmetric sums of operators acting on the coordinates of one, two, three, etc., particles, respectively. If equations for an effective three-particle operator with matrix elements $(ijk^{abc}|G|0)$ are not included explicitly, then it is not compatible with the variational principle to include matrix elements involving the corresponding determinants $\Phi_{ijk^{abc}}$ in determining the effective one- and two-particle operators.

In finite problems there is generally no simple expression for the integrals involved here which can be summed in closed form over a complete set of orbitals. In such cases a practicable procedure is to select a set of determinants indicated by perturbation theory [most conveniently treated in the form of Eqs. (8), (8'), etc.] to have the greatest effect on the true wave function and to solve the appropriate equations which diagonalize the many-particle Hamiltonian over this truncated basis. This produces a new trial wave function expressed as a linear combination of this truncated set. Further determinants can be added by iterating this procedure of estimating the contributions of individual determinants or linear combinations of them by perturbation methods and then diagonalizing exactly a matrix whose basis has been selected from functions which most affect the perturbation calculation.⁸

In such a procedure one would not ordinarily include all determinants of the form $\Phi_{ij^{ab}}$ before including any which involve three-particle transitions or more. For finite systems, whenever the total energy shift ΔE is small compared with the energy of doubly excited

states, the Brueckner method would be equivalent to doing just this. This is advantageous only if there is some convenient way to estimate the summations over complete sets of functions required in Eqs. (8), (8'), and (8''). The remainder of this paper will be restricted to consideration of the truncated set of determinants $\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}$.

III. CHOICE OF ORBITALS: HARTREE-FOCK CONDITION

The equations derived up to this point have been valid independently of any particular choice of the basic orbitals. However, if Φ_0 were simply an arbitrary determinant there would be no reason to expect the truncated set $\Phi_0, \Phi_i^a, \Phi_{ij}^{ab}$ to be an adequate basis for expansion of the true wave function. In the Hartree-Fock approximation one chooses Φ_0 to be the best single determinant. If this is expressed mathematically by choosing the set of occupied orbitals ϕ_i which makes $(0|H|0)$ stationary, then it turns out that for this basis of orbitals all matrix elements $(i^a|H|0)$ are identically zero.^{8,10}

In the Hartree-Fock basis the one-particle contributions to Eq. (8), and hence to the energy, vanish no matter how many higher order effects are taken into account. Hence the correction to the Hartree-Fock energy (of a single determinant as always in this discussion) can be expressed entirely by a two-particle operator with matrix elements equal to $(ij^{ab}|G|0)$. Since all $(i^a|H|0)$ vanish a first approximation to $(i^a|G|0)$ is zero. If this is substituted in Eqs. (8'') we have left just the equations arising from the truncated set of determinants Φ_0, Φ_{ij}^{ab} . These equations lead to an effective two-particle operator similar in nature to the Brueckner operator but derived in a basis of Hartree-Fock orbitals. This degree of approxi-

mation, including determinants Φ_0 and Φ_{ij}^{ab} in the Hartree-Fock basis, was taken into account in a previous analysis of the binding energy of light nuclei.¹¹

If G is thought of as an effective Hermitian two-particle operator,

$$G = \sum_{ij} u(i, j), \quad (10)$$

then the matrix elements in Eqs. (8), etc., can be expressed in terms of integrals over u and the operators T and v of the original Hamiltonian as follows:

$$(0|H|ij^{ab}) = (ij|v|ab)_N,$$

where

$$(wx|v|yz)_N \equiv (wx|v|yz) - (wx|v|zy),$$

$$(ij^{ab}|G|0) = (ab|u|ij)_N = (ij|u|ab)_N^*,$$

$$(ij^{cd}|H|ij^{ab}) = (cd|v|ab)_N,$$

$$(kl^{ab}|H|ij^{ab}) = (ij|v|kl)_N,$$

$$(jk^{bc}|H|ij^{ab}) = (ic|v|ak)_N \text{ if } c > b, k > j \text{ or } c < b, j < k \\ = -(ic|v|ak)_N \text{ if either } c < b \text{ or } k < j,$$

$$(jk^{ab}|H|ij^{ab}) = (i|T|k) + \sum_{l \neq j} (il|v|kl)_N \\ + (ib|v|kb)_N + (ia|v|ka)_N \text{ if } k > j \\ = \text{negative if } k < j.$$

$$(ij^{bc}|H|ij^{ab}) = (c|T|a) + \sum_{l \neq i, j} (cl|v|al)_N \\ + (cb|v|ab)_N \text{ if } c < b \\ = \text{negative if } c > b. \quad (11)$$

The Hartree-Fock condition on the basis of orbitals is

$$(i^a|H|0) = (a|T|i) + \sum_{l=1}^N (al|v|il)_N = 0 \\ \text{for all } i \leq N, a > N. \quad (12)$$

The equations derived from Eqs. (8), (8'') for the truncated set Φ_0, Φ_{ij}^{ab} are:

$$E = \sum_i (i|T|i) + \sum_{ij} (ij|v|ij)_N + \sum_{ij} \sum_{ab} \frac{(ij|v|ab)_N (ab|u|ij)_N}{E - D_{ij^{ab}}}, \quad (13)$$

$$(ab|u|ij)_N = (ab|v|ij)_N + \sum_{cd \neq a, b} \frac{(ab|v|cd)_N (cd|u|ij)_N}{E - D_{ij^{cd}}} + \sum_{kl \neq i, j} \frac{(kl|v|ij)_N (ab|u|kl)_N}{E - D_{kl^{ab}}}$$

$$+ \sum_{k \neq i, j} \sum_{c \neq a, b} \left\{ \frac{(ka|v|jc)_N (bc|u|ik)_N}{E - D_{ik^{bc}}} - \frac{(kb|v|jc)_N (ac|u|ik)_N}{E - D_{ik^{ac}}} \right. \\ \left. - \frac{(ka|v|ic)_N (bc|u|jk)_N}{E - D_{jk^{bc}}} + \frac{(kb|v|ic)_N (ac|u|jk)_N}{E - D_{jk^{ac}}} \right\}$$

$$+ \sum_{c \neq a, b} \left\{ \left[(b|T|c) + \sum_{l \neq i, j} (bl|v|cl)_N + (ba|v|ca)_N \right] \frac{(ac|u|ij)_N}{E - D_{ij^{ac}}} \right. \\ \left. - \left[(a|T|c) + \sum_{l \neq i, j} (al|v|cl)_N + (ab|v|cb)_N \right] \frac{(bc|u|ij)_N}{E - D_{ij^{bc}}} \right\}$$

$$+ \sum_{k \neq i, j} \left\{ \left[(k|T|i) + \sum_{l \neq i, j} (kl|v|il)_N + (ka|v|ia)_N + (kb|v|ib)_N \right] \frac{(ab|u|jk)}{E - D_{jk^{ab}}} \right. \\ \left. - \left[(k|T|j) + \sum_{l \neq i, j} (kl|v|jl)_N + (ka|v|ja)_N + (kb|v|jb)_N \right] \frac{(ab|u|ik)}{E - D_{ik^{ab}}} \right\}. \quad (14)$$

¹⁰ L. Brillouin, reference 1.

¹¹ R. K. Nesbet, Phys. Rev. 100, 228 (1955).

It should be noted that the operator formalism is applicable only to the first term of Eqs. (14) since the others are not in the form of matrix products. To simplify these equations it is convenient to introduce the Hartree-Fock single-particle Hamiltonian \mathcal{H}_0 , defined by its matrix elements

$$(m|\mathcal{H}_0|n) \equiv (m|T|n) + \sum_{l=1}^N (ml|v|nl)_N. \quad (15)$$

With this definition, formulas such as

$$(b|T|c) + \sum_{l \neq i, j} (bl|v|cl)_N = (b|\mathcal{H}_0|c) - (bi|v|ci)_N - (bj|v|cj)_N$$

can be used to reduce Eqs. (14) to

$$\begin{aligned} (ab|u|ij)_N &= (ab|v|ij)_N + \sum'_{cd} \frac{(ab|v|cd)_N (cd|u|ij)_N}{E - D_{ij}{}^{cd}} + \sum'_{kl} \frac{(kl|v|ij)_N (ab|u|kl)_N}{E - D_{kl}{}^{ab}} \\ &+ \sum'_k \sum'_c \left\{ \frac{(ka|v|jc)_N (bc|u|ik)_N}{E - D_{ik}{}^{bc}} - \frac{(kb|v|jc)_N (ac|u|ik)_N}{E - D_{ik}{}^{ac}} \right. \\ &\quad \left. - \frac{(ka|v|ic)_N (bc|u|jk)_N}{E - D_{jk}{}^{bc}} + \frac{(kb|v|ic)_N (ac|u|jk)_N}{E - D_{jk}{}^{ac}} \right\} \\ &+ \sum_{c \neq a, b} \left\{ \frac{(b|\mathcal{H}_0|c)(ac|u|ij)_N}{E - D_{ij}{}^{ac}} - \frac{(a|\mathcal{H}_0|c)(bc|u|ij)_N}{E - D_{ij}{}^{bc}} \right\} \\ &+ \sum_{k \neq i, j} \left\{ \frac{(k|\mathcal{H}_0|i)(ab|u|jk)_N}{E - D_{jk}{}^{ab}} - \frac{(k|\mathcal{H}_0|j)(ab|u|ik)_N}{E - D_{ik}{}^{ab}} \right\}. \quad (16) \end{aligned}$$

The primed summations include all values of indices $k < l \leq N$ and of $N < c < d$ with the exception of terms for which the denominator would be $E - D_{ij}{}^{ab}$.

The Hartree-Fock condition $(i^a|H|0) = 0$ is equivalent to $(a|\mathcal{H}_0|i) = 0$. Since Φ_0 is independent of any unitary transformation which does not mix occupied and unoccupied orbitals of Φ_0 we can choose a basis in which \mathcal{H}_0 is diagonalized for all orbitals, consistent with the Hartree-Fock condition. In this basis (the canonical Hartree-Fock basis), all terms in Eqs. (16) which involve \mathcal{H}_0 are zero.

Equations (16) are exact as they stand for the truncated basis $\Phi_0, \Phi_{ij}{}^{ab}$ independently of the Hartree-Fock condition. The principal effect of this condition is to remove the terms arising from determinants Φ_i^a from Eq. (8) for the energy and to justify neglecting such one-particle terms in Eqs. (8'').

IV. CHOICE OF ORBITALS: BRUECKNER CONDITION

One very great practical advantage of the Hartree-Fock condition is that it can be applied at a stage in the calculation when only a single determinant is under consideration, prior to solution of Eqs. (8), (8'), etc. It has the disadvantage that it does not completely remove the one-particle terms from Eqs. (8''). These terms can be removed at the expense of imposing a condition dependent on the solution of Eqs. (8) and (8'') by requiring that

$$(i^a|G|0) = 0 \text{ for all } i \leq N, a > N. \quad (17)$$

This will be referred to as the "Brueckner condition" since it has essentially the same effect as the auxiliary condition which determines the basis of orbitals in various statements of the Brueckner method.¹²

Under the Brueckner condition the equations for the many-particle basis $\Phi_0, \Phi_i^a, \Phi_{ij}{}^{ab}$ reduce to

$$\begin{aligned} E &= (0|H|0) + (0|G|0) \\ &= (0|H|0) + \sum_{ij} \sum_{ab} \frac{(0|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}{}^{ab}}, \quad (18) \end{aligned}$$

$$\begin{aligned} (i^{a'}|G|0) &= (i^{a'}|H|0) \\ &+ \sum_{ij} \sum_{ab} \frac{(i^{a'}|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}{}^{ab}} = 0, \quad (19) \end{aligned}$$

$$\begin{aligned} (i'j, a'b'|G|0) &= (i'j, a'b'|H|0) \\ &+ \sum_{ij} \sum_{ab} \frac{(i'j, a'b'|H|ij^{ab})(ij^{ab}|G|0)}{E - D_{ij}{}^{ab}}. \quad (20) \end{aligned}$$

The diagonal matrix elements of H are to be omitted from Eqs. (20).

If G is thought of as an effective Hermitian two-particle operator

$$G = \sum_{ij} t(i, j), \quad (21)$$

¹² K. A. Brueckner and W. Wada, reference 4; H. A. Bethe, reference 6, Sec. III.

which differs from the operator u defined in Eq. (10) because of the different conditions on the orbital basis, Eqs. (18)–(20) can be expressed in terms of integrals over the operators t , T , and v by use of the expressions in Eqs. (11). Equation (18) for the energy reduces to Eq. (13) with u replaced by the Brueckner operator t and Eqs. (20) reduce to Eqs. (14) or (16) with the same replacement. The principal change is that the Hartree-Fock condition, Eq. (12), equivalent to $(a|\mathcal{H}_0|i)=0$, is replaced by the Brueckner condition (19) which reduces to

$$0 = (a|\mathcal{H}_0|i) + \sum_j \sum_{bc} \frac{(aj|v|bc)_N (bc|t|ij)_N}{E - D_{ij}{}^{bc}} + \sum_{jk} \sum_b \frac{(jk|v|ib)_N (ba|t|jk)_N}{E - D_{jk}{}^{ba}} + \sum_{j \neq i} \sum_{b \neq a} \frac{(j|\mathcal{H}_0|b)(ab|t|ij)_N}{E - D_{ij}{}^{ab}}. \quad (22)$$

The summations include all values of $j < k \leq N$ and $N < b < c$. Again it should be noted that the operator formalism is not applicable to the third set of terms of Eqs. (22) since they are not in the form of matrix products.

Equations (22) can formally be set equal to matrix elements of an effective one-particle operator $(a|\mathcal{G}_0|i)$. The usual statement of the Brueckner condition is that the basis orbitals should be eigenfunctions of the effective operator \mathcal{G}_0 .¹³ This implies Eqs. (22) but is an unnecessarily strong condition for simplifying Eqs. (8), etc.

In the calculations to date on infinite uniform matter¹³ both conditions (22) and (12) are identically satisfied for plane-wave orbitals by conservation of momentum. Hence the Brueckner condition has not yet actually been applied. In such cases there is no difference between the effective operators u and t .

In calculations on finite systems conditions (12) and (22) will not in general be compatible. Hence the one-particle matrix elements in Eqs. (22) and (14) or (16) will not vanish under the Brueckner condition even though they can be made to vanish by a transformation of orbitals compatible with the Hartree-Fock condition. It would be necessary to take such matrix elements into account in applying the Brueckner method to finite systems.

V. DISCUSSION

Since no effective three-particle operator is considered in the Brueckner method, for small ΔE the trial wave function is a linear combination of determinants Φ_0 , Φ_i^a , $\Phi_{ij}{}^{ab}$. The effect of the condition (12) or (22) is to exclude the determinants Φ_i^a . In the Hartree-Fock case, applied to a ground state, the determinant ${}_{HF}\Phi_0$

is that of minimum energy. Application of Eqs. (13) and (16) can only improve this energy, since they are equivalent to increasing the trial basis from Φ_0 to Φ_0 , $\Phi_{ij}{}^{ab}$. Hence a calculation in the Hartree-Fock orbital basis, using the effective operator u [Eq. (10)] would necessarily obtain a better energy and wave function than the Hartree-Fock result. A further improvement could be assured by choosing the orbital basis which obtains the best energy from diagonalizing the Hamiltonian over the set ${}_M\Phi_0$, ${}_M\Phi_{ij}{}^{ab}$ in that orbital basis. Here the subscript M is used to refer to this basis.

The wave function implied for small ΔE by use of the Brueckner effective two-particle operator t is also a linear combination of some ${}_B\Phi_0$ and ${}_B\Phi_{ij}{}^{ab}$ in the Brueckner basis. It can be shown that the Brueckner condition (22) is not identical with the condition required to minimize the energy of a function of this form.¹⁴ Hence, unless there is an accidental degeneracy, the single determinant ${}_B\Phi_0$ has necessarily a higher energy than ${}_{HF}\Phi_0$, since the energy of the latter is minimized, and the best linear combination of ${}_B\Phi_0$ and ${}_B\Phi_{ij}{}^{ab}$ has a higher energy than the best function of this form (a linear combination of ${}_M\Phi_0$ and ${}_M\Phi_{ij}{}^{ab}$). The energy of the best linear combination of ${}_{HF}\Phi_0$ and ${}_{HF}\Phi_{ij}{}^{ab}$ must lie somewhere between that of ${}_{HF}\Phi_0$ and the best linear combination of ${}_M\Phi_0$ and ${}_M\Phi_{ij}{}^{ab}$. Unfortunately, since the set ${}_B\Phi_0$, ${}_B\Phi_{ij}{}^{ab}$ is far from complete, it is not possible to prove that the best linear combination of ${}_B\Phi_0$ and ${}_B\Phi_{ij}{}^{ab}$ has an energy below that of the single Hartree-Fock determinant ${}_{HF}\Phi_0$, nor *a fortiori* below that of the best combination of ${}_{HF}\Phi_0$ and ${}_{HF}\Phi_{ij}{}^{ab}$. Unless some further proof can be given, the relative validity of calculations equivalent to superposition of configurations Φ_0 and $\Phi_{ij}{}^{ab}$ based on the Brueckner condition (22) and on the Hartree-Fock condition (12) can only be decided empirically.

Since the Brueckner condition always can be satisfied by a basis of plane waves, corresponding to uncoupled particles for a finite system, it would be of great importance to establish the existence of other nontrivial solutions, as has been done empirically for the Hartree-Fock condition, before applying this condition to problems in which for practical reasons one must work with an arbitrary finite set of orbitals and thus be forced to truncate the summations in Eqs. (13), (16), and (22). Otherwise there would be danger of converging to the trivial solution, if it should be unique.

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APPENDIX I. REACTION MATRIX

Consider a matrix eigenvalue equation,

$$\sum_\nu H_{\mu\nu} c_\nu = E c_\mu. \quad (A-1)$$

¹⁴ See Appendix II.

¹³ See reference 4 and H. A. Bethe, reference 6, Sec. XI.

If $H_{\mu\nu}$ is divided into a purely diagonal matrix $D_\mu = H_{\mu\nu}\delta_{\mu\nu}$ and matrix with no diagonal elements $N_{\mu\nu} = H_{\mu\nu}(1-\delta_{\mu\nu})$, this can be written

$$\sum_\nu N_{\mu\nu}c_\nu = (E - D_\mu)c_\mu. \quad (\text{A-2})$$

Now define

$$G_{\mu 0} \equiv (E - D_\mu)c_\mu. \quad (\text{A-3})$$

Then the eigenvalue equation becomes

$$G_{\mu 0} = \sum_\nu \frac{N_{\mu\nu}G_{\nu 0}}{E - D_\nu}. \quad (\text{A-4})$$

If the eigenvector is normalized so that $c_0 = 1$, this is equivalent to the inhomogeneous equations

$$G_{\mu 0} = N_{\mu 0} + \sum_{\nu \neq 0} \frac{N_{\mu\nu}G_{\nu 0}}{E - D_\nu}, \quad (\text{A-5})$$

under an auxiliary condition which determines the eigenvalue E ,

$$E - D_0 = G_{00} = \sum_{\nu \neq 0} \frac{N_{0\nu}G_{\nu 0}}{E - D_\nu}. \quad (\text{A-5}')$$

The numbers $G_{\mu 0}$ can be thought of as the first column of a matrix called the "reaction matrix."

APPENDIX II. CONDITION FOR STATIONARY ENERGY

For an arbitrary function Ψ , the mean value of the energy will be stationary for variations $\delta\Psi$ if

$$(\delta\Psi|H|\Psi) = 0. \quad (\text{A-6})$$

If Ψ is a linear combination $\Phi_0 + \sum C_{ij}{}^{ab}\Phi_{ij}{}^{ab}$, then if the energy is stationary for all variations of the set of orthonormal orbitals which retain the orthonormality property, (A-6) must hold for the particular variation

$$\delta\phi_{i'} = d\alpha \cdot \phi_{a'}; \quad \delta\phi_{a'} = -d\alpha \cdot \phi_{i'}, \quad (\text{A-7})$$

where only two orbitals are changed.

For this variation,

$$\frac{1}{d\alpha} \delta\Psi = \Phi_{i',a'} + \sum_{ij \neq i'} \sum_{ab \neq a'} C_{ij}{}^{ab} \Phi_{ij}{}^{a'b} - \sum_{ij \neq i'} \sum_{b \neq a'} C_{i'j}{}^{a'b} \Phi_{ij}{}^b. \quad (\text{A-8})$$

The self-consistency condition Eqs. (19), (22) is

$$({}_{i'}^{a'}|H|\Psi) = 0.$$

This is not equivalent to (A-6) since it neglects matrix elements between Ψ and determinants $\Phi_{i'ij}{}^{a'ab}$ and Φ_j^b which occur in (A-8). This has no effect in the case of the infinite nucleus of uniform density, since all these matrix elements are identically zero for plane-wave orbitals.

The actual self-consistency condition of Brueckner differs from (20) by one detail which cancels out some of the matrix elements arising from (A-8). The Brueckner formula represents matrix elements

$$({}_{i'}^{a'}|H|{}_{i'}^{a'b}) = (j|T|b) + \sum_{i \neq i'} (ij|v|ib)_N + (a'j|v|a'b)_N \quad (\text{A-9})$$

simply by

$$({}_{i'}^{a'}|v|a'b)_N. \quad (\text{A-10})$$

Now in the expansion of $(1/d\alpha)(\delta\Psi|H|\Psi)$ these matrix elements occur as

$$\sum_{j \neq i'} \sum_{b \neq a'} C_{i'j}{}^{a'b} ({}_{i'}^{a'}|H|{}_{i'}^{a'b}). \quad (\text{A-11})$$

But there is another term in the expansion, due to determinants Φ_j^b ,

$$- \sum_{j \neq i'} \sum_{b \neq a'} C_{i'j}{}^{a'b} (j^b|H|0), \quad (\text{A-12})$$

where

$$(j^b|H|0) = (j|T|b) + \sum_{i \neq i'} (ij|v|ib)_N + (i'j|v|i'b)_N. \quad (\text{A-13})$$

Hence each term in the combination of (A-9) and (A-13) reduces to

$$({}_{i'}^{a'}|v|a'b)_N - (i'j|v|i'b)_N, \quad (\text{A-14})$$

which may be compared with (A-10).

All other matrix elements between (A-8) and Ψ involve the coefficients $C_{ij}{}^{ab}$ quadratically. If they are small, it can be argued that the Brueckner self-consistency condition is an approximation to the condition of stationary energy.