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Maximum-Overlap Orbitals, an Energy Variational Principle, and Perturbation Theory

Donald H. Kobe

Department of Physics, North Texas State University, Denton, Texas 76203

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The maximum-overlap orbitals first proposed by Brenig, in which the overlap between the true wave function and a Slater determinant is maximized, is shown to be equivalent to Löwdin's exact self-consistent-field theory. By defining an energy functional and varying it, some points in Löwdin's theory are clarified. The ground-state energy is expanded in perturbation theory, and it is pointed out that some diagrams could become divergent. In order to eliminate these diagrams, Bogoliubov's principle of compensation of dangerous diagrams (PCDD) is extended to finite fermion systems. In these systems, the PCDD states that the sum of all the diagrams leading from the vacuum to a single particle-hole state must be set equal to zero. This condition is the Brillouin-Brueckner condition, which is also obtained from the other methods. The form of the PCDD obtained here is different from another form that leads to Löwdin's natural orbitals, and the difference is discussed.

I. INTRODUCTION

One of the fundamental problems of many-body quantum theory is the reason for the success of the shell model for nuclei.[1] For atoms, the shell structure is simply explained by Hartree-Fock (HF) theory,[2] which reduces the system of many electrons interacting with each other and the nucleus to a system of independent particles moving in the average field produced by other particles. In the nuclear case, the average field due to the other nucleons becomes infinite in HF theory when the usual hard-core nuclear potentials[3] are used.

In order to surmount the difficulties associated with hard-core potentials, Brueckner and co-workers[4] developed the reaction-operator (or t-matrix) approach. Instead of considering a single nucleon moving in the average field of all the others, they considered the interaction of two nucleons in the average field of the remaining nucleons.[5] This "effective interaction" is then substituted into the HF equations for finite systems, which must be solved self-consistently with a Lippmann-Schwinger[6]-like equation for the two-body reaction operator (or t matrix).[7] In order to test these ideas, they have been tried on nuclear matter in which the wave functions are plane waves.[7,8] Only recently have some double-self-consistent Brueckner-HF-theory calculations been carried out.[9]

Even though Brueckner and Goldman[10] attempted to find an energy variational basis for their theory,[11] their approach contains a serious error, first pointed out by Brandow.[12] They varied a perturbation expansion of the ground-state energy and obtained equations similar to the HF equations with the potential replaced by the "t matrix," and an additional "rearrangement potential." However, the perturbation expansion is not an expectation value of the Hamiltonian with some trial wave function, so no Rayleigh-Ritz principle exists. Hence, there is no justification for the variation. The double-self-consistency idea of Brueckner-HF theory was nevertheless retained because, in Brown's words, "of the intuitive feeling, . . . , that self-consistency is a 'good' thing."[13] The alternative to self-consistency is not necessarily inconsistency. It is possible to be consistent without being self-consistent, as for example in the case of those who advocate using any complete set of basis functions and calculating all the diagrams occurring in

perturbation theory.[14]

In the absence of any sound variational principle for determining the orbitals, Kirson,[15] following Brandow,[16] proposed the "method of maximal cancellation of self-energy insertions" to determine the shell-model potential and hence the orbitals. The mathematical complications associated with this procedure are formidable,[17] since extreme care must be taken not to overcount diagrams. In fact, in a recent paper, Brandow[18] has discovered some over-counting in previous work[16] and has introduced appropriate "over-counting corrections." Kirson[15] stated that this method will lead to the most-rapid convergence of the perturbation expansion, but has since altered his point of view.[19]

In a previous paper[20] it was shown that in the perturbation expansion of the ground-state energy, there are some diagrams which could become divergent in arbitrarily high order. In order to eliminate these diagrams, Bogoliubov's *principle of compensation of dangerous diagrams* (PCDD), first used in the theory of superconductivity and superfluidity[21] was extended to finite fermion systems. The sum of all the diagrams leading from the vacuum to a single particle-hole state was set equal to zero. This procedure was shown to lead to Löwdin's natural orbitals,[22] which satisfy a number of variational properties.

In this paper, it will be shown that by using a simple expression for the ground-state energy,[23] which is obtained using a Slater determinant as a model wave function,[24] the application of Bogoliubov's PCDD leads to orbitals which have the maximum overlap between the true wave function and a Slater determinant. This criterion for choosing the orbitals was first proposed by Brenig[25] as an alternative to HF theory. It is still valid even if the potential has a hard core, whereas HF theory is not. If the overlap is maximized, the condition obtained is that the true wave function cannot contain any singly excited configurations.[26]

The vanishing of the singly excited configurations is equivalent to the condition obtained by Löwdin in his exact self-consistent-field (ESCF) theory which he called the *Brillouin-Brueckner condition*.[27] It is analogous to the Brillouin condition of HF theory,[28] except that the perturbing potential is replaced by the corresponding reaction operator.[23]

The fact that the PCDD can be used to justify both the maximum-overlap orbitals and the natural orbitals should be no cause for alarm. Bogoliubov's original prescription[21] was in terms of diagrams which eliminated divergences from the perturbation expansion of the ground-state energy. Diagrams can be defined differently depending on the formalism used. The reaction-operator formalism used in this paper to obtain the maximum-overlap orbitals corresponds to the "model description."[24] It thus corresponds to the PCDD (I) discussed for superconductivity[29] and superfluidity.[30] On the other hand, the natural orbitals discussed in the previous paper[20] occur in the "true description" and it corresponds to the PCDD (II) in superconductivity[31] and superfluidity.[32] A Green's-function formalism is most applicable to the true description.[33] The expression for the ground-state energy is simpler in the model description presented here, however.[34] The natural and maximum-overlap orbitals have been compared by Kutzelnigg and Smith.[35]

In Sec. II, the salient features for our purposes of HF theory will be pointed out and the notation established. In Sec. III Löwdin's ESCF theory[23] is clarified with the help of an energy functional. It leads to the Brillouin-Brueckner condition. The condition of maximum overlap, discussed in Sec. IV, leads to the same condition. In Sec. V the PCDD is applied to the ground-state energy in the "model" description, and is also shown to lead to the same condition. Thus, all these formulations are equivalent. The conclusion gives a comparison of the maximum-overlap orbitals with HF orbitals.

II. HARTREE-FOCK THEORY

HF theory is so well known[2] it seems hardly necessary to discuss it again. However, a few salient points of HF theory will be mentioned, in order to show how it can be systematically generalized to systems in which the HF self-consistent-field (SCF) does not exist, as for example, in systems of particles with hard cores. The notation used in the remainder of the paper will also be established in a familiar context.

For a system of fermions interacting with a two-body potential v, the Hamiltonian is

$$H = T + v . \tag{2.1}$$

The single-particle operator T is

$$T = \sum_{\alpha\beta} \langle \alpha | T | \beta \rangle a_\alpha^\dagger a_\beta , \tag{2.2}$$

which is the sum of the kinetic energy operator and a single-particle potential, if it is present. The two-body potential is

$$v = \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | v | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta . \tag{2.3}$$

In Eqs. (2.2) and (2.3) the $a_\alpha^\dagger$ and a_β are the creation and annihilation operators for particles in the states ϕ_α and ϕ_β, respectively.[36] They satisfy the usual fermion anticommutation relations. The matrix elements are calculated in the representation $\phi = \{\phi_\alpha\}$, and the one in Eq. (2.3) is antisymmetrized.

To Eq. (2.1) a single-particle operator

$$U=\sum_{\alpha\beta}\langle\alpha|U|\beta\rangle a_\alpha{}^\dagger a_\beta \tag{2.4}$$

and a constant E can be added to give

$$H=H_0+V. \tag{2.5}$$

The unperturbed Hamiltonian H_0 is

$$H_0=E+T+U, \tag{2.6}$$

and the perturbation V is

$$V=v-U-E. \tag{2.7}$$

The problem of the independent-particle model is to choose the best eigenfunctions, in some sense, of H_0.

In HF theory, the unperturbed wave function is chosen to be a Slater determinant:

$$\Phi_0=\prod_{i=1}^{N} a_i{}^\dagger|\text{vac}\rangle. \tag{2.8}$$

The state $|\text{vac}\rangle$ is the vacuum state of no particles.

The creation operator $a_i{}^\dagger$ is defined in terms of the orbital ϕ_i and the field operator $\psi^\dagger(x)$ such that

$$a_i{}^\dagger=a^\dagger(\phi_i)=\int dx\,\phi_i(x)\psi^\dagger(x). \tag{2.9}$$

The field operators $\psi^\dagger(x)$ and $\psi(y)$ create and annihilate a particle at the space-spin points x and y, respectively, which correspond to particles with unphysical δ-function wave functions. Even though Frenkel[37] anticipated a generalization of HF theory, he formally varied the field operators. Since a δ function would have to be varied, it is difficult to understand in what space of functions the variations are made.

The orbitals used in Eq. (2.8) are such that the Slater determinant Φ_0 is an eigenstate of the unperturbed Hamiltonian

$$H_0\Phi_0=E_0\Phi_0, \tag{2.10}$$

where the unperturbed energy is E_0. The problem is to determine the best choice of U and E in Eq. (2.6).

The criterion of best orbitals in HF theory is that the unperturbed ground-state energy is

$$H_{00}[\phi]=\langle\Phi_0|(H_0+V)|\Phi_0\rangle=\min, \tag{2.11}$$

which is schematically shown in Fig. 1. Because of the Rayleigh-Ritz variational principle, this energy is always greater than the true ground-state energy, $\mathcal{E}_0$.

The variation of Eq. (2.11) subject to the constraint of orthonormality results in the Brillouin condition[28]

$$\langle\Phi_0|V|\Phi_i^a\rangle=0, \quad i\in\text{FS}, \quad a\notin\text{FS}. \tag{2.12}$$

The singly excited configuration Φ_i^a is defined as

$$\Phi_i^a=a_a{}^\dagger a_i\Phi_0. \tag{2.13}$$

where i is any occupied state, i.e., in the Fermi sea (FS) and a is any unoccupied state, i.e., out of the FS. The Brillouin condition is shown graphically in Fig. 2. This figure is generalized in Sec. III.

III. EXACT SELF-CONSISTENT-FIELD THEORY

The HF theory of Sec. II has been generalized by Löwdin in his ESCF theory.[23] In his original paper, Löwdin varied an expression for the true ground-state energy, which is independent of the choice of orbitals, as he pointed out.[38] He obtained HF-like equations, but without the so-called "rearrangement potential." In this section it is explained how Löwdin's procedure can be justified in a mathematically rigorous way by varying an energy functional, which also enables a comparison with HF theory to be made. The procedure also justifies the use of the word "exact" in the ESCF theory. This method is similar in spirit to a variational principle used by Eden, Emery, and Sampanthar,[39] which did not lead to a "rearrangement potential"[10] either.

The true ground-state energy $\mathcal{E}_0$ is the solution of the Schrödinger equation

$$H\Psi=\mathcal{E}_0\Psi, \tag{3.1}$$

where Ψ is the true ground-state wave function. If the full many-body reaction operator t is defined by[40]

$$t\Phi_0=V\Psi \tag{3.2}$$

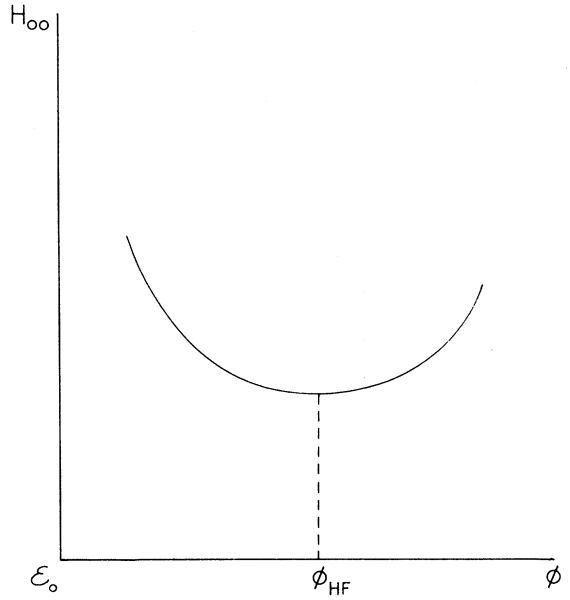

FIG. 1. A schematic plot of the ground-state energy in HF theory. The abscissa represents a multidimensional function space.

and intermediate normalization

$$\langle\Psi|\Phi_0\rangle = 1 \tag{3.3}$$

is used, the true ground-state energy can be written as

$$\mathcal{E}_0 = \langle\Phi_0|(H_0+t)|\Phi_0\rangle . \tag{3.4}$$

Equation (3.4) is analogous to Eq. (2.11). The full reaction operator t has been shown to satisfy a Lippmann-Schwinger equation[40]

$$t = V + VG_0t . \tag{3.5}$$

The reduced resolvent operator G_0 is defined symbolically as

$$G_0 = \frac{1-|\Phi_0\rangle\langle\Phi_0|}{\mathcal{E}_0 - H_0}, \tag{3.6}$$

and has been defined more precisely by Löwdin.[41]

The true ground-state energy is a constant, independent of the choice of orbitals, even though both Φ_0 and H_0+t are functionals of $\phi = \{\phi_\alpha\}$. For a given Slater determinant $\Phi_0[\phi]$, the reaction operator t calculated from Eq. (3.5) is also a functional of ϕ such that Eq. (3.4) is satisfied.

However, Eq. (3.4) can be used to define a functional of two sets of orbitals $\phi = \{\phi_\alpha\}$ and $\chi = \{\chi_\alpha\}$,

$$\mathcal{E}[\phi,\chi] = \langle\Phi_0[\phi]|(H_0[\chi]+t[\chi])|\Phi_0[\phi]\rangle . \tag{3.7}$$

This functional has the property that when $\phi = \chi$, the true ground-state energy is obtained,

$$\mathcal{E}[\phi,\phi] = \mathcal{E}[\chi,\chi] = \mathcal{E}_0 , \tag{3.8}$$

because of Eq. (3.4). The functional $\mathcal{E}[\phi,\chi]$ can be varied with respect to ϕ keeping χ fixed:

$$\delta_\phi\mathcal{E}[\phi,\chi] = 0 , \tag{3.9}$$

which determines the extremum of the functional for fixed χ. In principle, this condition can be used to determine the orbitals ϕ as functionals of χ,

$$\phi = \phi[\chi] . \tag{3.10}$$

Although not necessary to the argument, the extremum can be assumed, without loss of generality, to be a minimum. The extremum is thus

$$\min\mathcal{E} = \mathcal{E}[\phi[\chi],\chi] . \tag{3.11}$$

This variational principle is not a Rayleigh-Ritz principle, so the extremum can be anywhere. Of course the Rayleigh-Ritz principle gives an energy which must lie *above* the true ground-state energy $\mathcal{E}_0$. In our variational principle, however, the set χ can be chosen such that the minimum is *equal* to the true ground-state energy,

$$\mathcal{E}[\phi[\chi],\chi] = \mathcal{E}_0 . \tag{3.12}$$

This condition obtains if

$$\phi[\chi] = \chi , \tag{3.13}$$

as can be seen from Eq. (3.8). Equation (3.12) is shown schematically in Fig. 3.

To obtain the situation in Eq. (3.12), the condition in Eq. (3.13) is imposed on Eq. (3.9) after the variation has been performed:

$$\delta_\phi\mathcal{E}[\phi,\chi]|_{\phi=\chi} = 0 . \tag{3.14}$$

If the functional form of $\mathcal{E}[\phi,\chi]$ given in Eq. (3.7) is used, Eq. (3.14) gives

$$\langle\Phi_0|t|\Phi_i^a\rangle = 0 , \quad i\in\mathrm{FS} , \quad a\notin\mathrm{FS} . \tag{3.15}$$

Löwdin[27] called this condition the *Brillouin-Brueckner condition*, since it is the natural generalization of the Brillouin condition for HF theory given in Eq. (2.12). A condition like this, but with only the two-body part of the reaction operator, was first called by Nesbet[42] the Brueckner condition. Löwdin uses the full reaction operator defined in Eq.

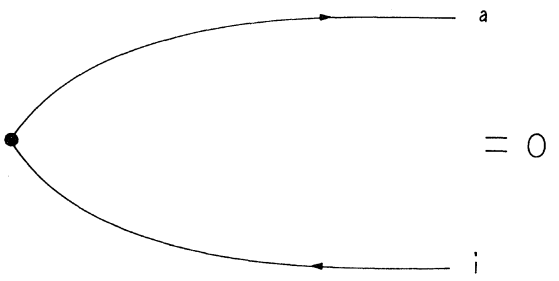

FIG. 2. The Brillouin condition of Eq. (2.12) in graphical form. The state $i\in$ FS and $a\notin$ FS.

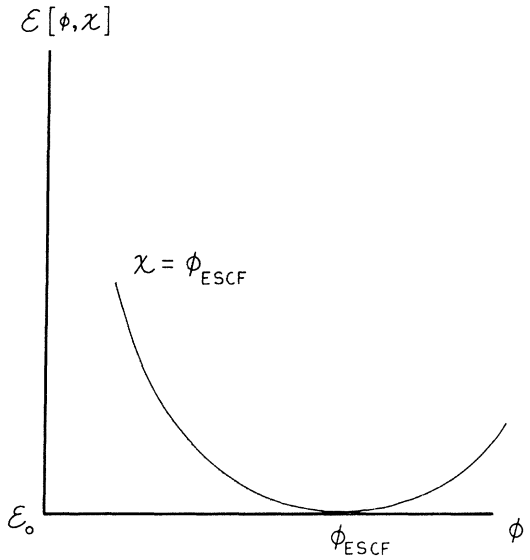

FIG. 3. A schematic plot of the energy functional $\mathcal{E}[\phi,\chi]$ when the minimum occurs at $\mathcal{E}_0$.

(3.2). The Brillouin-Brueckner condition is shown graphically in Fig. 4, and can be seen to be the natural generalization of Fig. 2.

The derivation of the Brillouin-Brueckner condition given here has the advantage of clearly showing the connection between HF and ESCF theory in Figs. 1 and 3, and Figs. 2 and 4. The reason for the word "exact" in the ESCF theory is also clearly shown in Fig. 3. The condition in Fig. 3 is optimum, since a first-order change in the wave function Φ_0 would cause only a second-order change from the true ground-state energy if the true reaction operator t is used. Conversely, if the orbitals used to calculate the true reaction operator are varied in first order, only a second-order change will be made in the energy.[43]

There has been much confusion in the literature regarding the so-called "rearrangement potential."[44] In their original paper, Brueckner and Goldman[10] varied an expression for the approximate ground-state energy using an equation similar to Eq. (3.4), but with only the two-body part of the reaction operator. They not only varied the Slater determinant, but varied the reaction operator as well. The term obtained by varying the reaction operator was called the "rearrangement potential," which was said to be related to the rearrangement energy of previous work.[45] The rearrangement energy was needed for agreement with the Hugenholtz–Van Hove theorem.[46] An alternative proof of the theorem has been given by Villi.[47] Since the expression Brueckner and Goldman varied was not of the form of the expectation value of the Hamiltonian with respect to a trial wave function, there is no Rayleigh-Ritz principle.[12] Thus there is no justification for the variation, since the variation might give further departure from the true ground-state energy. This procedure was also used by Brandow,[48] who later gave it up.[12, 18, 49]

The terms "rearrangement potential" and "rearrangement energy" continue to be used, however, in other senses which are legitimate.[50] Thus in much work the "rearrangement potential" is merely the contribution of some additional diagrams added to the perturbation expansion of the shell-model potential.[51] The rearrangement energy is just higher-order contributions to the perturbation expansion of the ground-state energy.[52, 53]

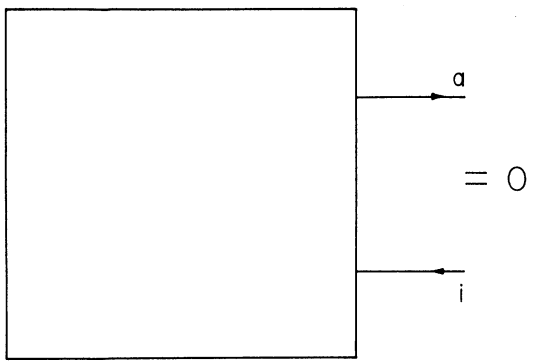

FIG. 4. The Brillouin-Brueckner condition of Eq. (3.15) in graphical form. The state $i \in$ FS and $a \notin$ FS.

The most recent reaction-operator calculation on finite nuclei[54] also uses the variational principle of Brueckner and Goldman[10] to obtain the rearrangement potential, which is shown to be important in obtaining saturation. However, the rearrangement potential is approximated by an expression of the same form as the self-consistent potential, and is absorbed into it. On the other hand, the effective interaction is adjusted to give the proper binding in nuclear matter. Thus it is possible that a proper calculation of the two-, three-, ... body parts of the reaction operator t used here would give results similar to Negele's, without using the rearrangement potential obtained by varying the effective interaction.

IV. MAXIMUM OVERLAP ORBITALS

Another criterion that can be used to determine the orbitals in a many-fermion system even when HF theory breaks down is that the distance in Hilbert space between the true ground-state wave vector Ψ and the Slater determinant Φ_0

$$\|\Psi - \Phi_0\| = \min . \tag{4.1}$$

If this condition is expanded and the phases are chosen properly, it can be shown to be equivalent[35] to the condition of maximum overlap,

$$\langle \Psi | \Phi_0 \rangle = \max , \tag{4.2}$$

which was first proposed by Brenig[25] as a criterion for choosing the orbitals when HF theory breaks down.

If the variation of Eq. (4.2) is performed, the result is

$$\langle \Psi | \Phi_i^a \rangle = 0 , \quad i \in \mathrm{FS} , \ a \notin \mathrm{FS} , \tag{4.3}$$

which states that singly excited configurations do not contribute to the true ground-state wave function.[26] This condition has been used by Coester[55] in his theory of finite fermion systems, without mentioning that it follows from the above variational principles.

The condition obtained in Eq. (4.3) is, moreover, completely equivalent to the Brillouin-Brueckner condition obtained in Eq. (3.15). The true wave operator W is defined as[40]

$$W\Phi_0 = \Psi . \tag{4.4}$$

Since Ψ can contain complicated correlations, it is

obvious that W must be a sum of many-body operators. In the derivation of the Lippmann-Schwinger equation in Eq. (3.5), it was first established that the wave operator satisfies the equation[40]

$$W = 1 + G_0 t . \tag{4.5}$$

When Eq. (4.4) is substituted into Eq. (4.3) and use is made of Eq. (4.5), the result is

$$\langle \Phi_0 | t G_0 | \Phi_i^a \rangle = 0 . \tag{4.6}$$

Since Φ_i^a is an eigenfunction of H_0, Eq. (4.6) reduces to the Brillouin-Brueckner condition of Eq. (3.15). The equivalence of the maximum-overlap criterion and the ESCF is thus established.

V. PRINCIPLE OF COMPENSATION OF DANGEROUS DIAGRAMS

In addition to showing that the maximum-overlap orbitals are equivalent to the ESCF theory, we will show that an extension of Bogoliubov's PCDD, first used in superconductivity and superfluidity theory,[21] to finite fermion systems also leads to the same conclusion. In previous publications on the PCDD, two different forms of the PCDD, called the PCDD (I)[29,30] and PCDD (II),[31,32] were found. They differed somewhat in their analytical expression, but not in their graphical representation. A previous paper on finite fermion systems showed that the natural orbitals of Löwdin are given by a condition that corresponds to the PCDD (II).[20] In this section it is shown that the maximum-overlap orbitals are given by a condition that corresponds to the PCDD (I).

The orbitals used in the construction of the Slater determinant in Eq. (2.8) are eigenfunctions of the single-particle operator h:

$$h\phi_\alpha = \epsilon_\alpha \phi_\alpha , \tag{5.1}$$

which is a sum of the single-particle operators

$$h = T + U + E/N , \tag{5.2}$$

where N is the number of particles in the system.

The potential U and the constant E are as yet undetermined. They will be chosen in this section in such a way as to eliminate potentially divergent terms from the perturbation expansion of the ground-state energy. In the representation of Eq. (5.1) the many-body Hamiltonian H_0 in Eq. (2.6) is in diagonal form

$$H_0 = \sum_\alpha \epsilon_\alpha a_\alpha^\dagger a_\alpha . \tag{5.3}$$

The resolution of the identity in terms of zero-, singly, doubly, ..., N-excited configurations is

$$1 = |\Phi_0\rangle\langle\Phi_0| + \sum |\Phi_i^a\rangle\langle\Phi_i^a| + \sum |\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}| + \cdots + \sum |\Phi_{ij\cdots k}^{ab\cdots c}\rangle\langle\Phi_{ij\cdots k}^{ab\cdots c}| , \tag{5.4}$$

where the sums are over all $i, j, \ldots, k \in$ FS, and $a, b, \ldots, c \notin$ FS. The last term in Eq. (5.4) is an N-excited configuration. The general term in Eq. (5.4) is an n-excited configuration ($n = 0, 1, 2, 3, \ldots, N$) consisting of n particle-hole pairs. It is obtained by applying n annihilation operators for occupied states to Φ_0, thus creating n holes, and then applying n creation operators for unoccupied states. A general term in Eq. (5.4) can be written as

$$\Phi_{ij\cdots k}^{ab\cdots c} = a_a^\dagger a_b^\dagger \cdots a_c^\dagger a_i a_j \cdots a_k \Phi_0 \tag{5.5}$$

for $i, j, \ldots, k \in$ FS and $a, b, \ldots, c \notin$ FS.

The true ground-state energy is given by Eq. (3.4). The Lippmann-Schwinger equation in Eq. (3.5) can be substituted into Eq. (3.4), and the resolution of the identity in Eq. (5.4) can be used. The result for the difference between the true ground-state energy and the unperturbed energy is

$$\begin{aligned} \mathcal{E}_0 - E_0 &= \langle \Phi_0 | t | \Phi_0 \rangle \\ &= \langle \Phi_0 | V | \Phi_0 \rangle + \sum \frac{\langle \Phi_0 | V | \Phi_i^a \rangle \langle \Phi_i^a | t | \Phi_0 \rangle}{D_i^a} \\ &\quad + \sum \frac{\langle \Phi_0 | V | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | t | \Phi_0 \rangle}{D_{ij}^{ab}} , \end{aligned} \tag{5.6}$$

where the sum is over all $i, j \in$ FS, and $a, b \notin$ FS. Since the excited configurations are eigenstates of H_0, the energy denominators are

$$D_i^a = \mathcal{E}_0 - (E_0 + \epsilon_a - \epsilon_i) \tag{5.7}$$

and

$$D_{ij}^{ab} = \mathcal{E}_0 - (E_0 + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) , \tag{5.8}$$

for the singly and doubly excited configurations, respectively. There are no more terms in Eq. (5.6), since the operator V can connect at most a doubly excited configuration with the ground-state Φ_0.

Figure 5 shows the graphical representation of the energy shift in Eq. (5.6). In order to interpret Fig. 5, the correspondence between the mathematical quantities and graphical quantities shown in Fig. 6 must be used.

If the arbitrary parameter E which was introduced in Eqs. (2.6) and (2.7) is chosen to be zero, then the energy denominators in Eqs. (5.7) and (5.8) are of the Brillouin-Wigner type.[56] The expression

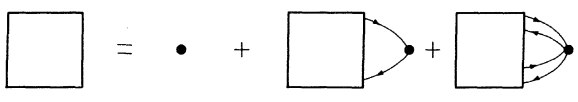

FIG. 5. The graphical representation of the energy shift of Eq. (5.6). A sum is implied over the intermediate states. For the definition of the diagrams see Fig. 6.

for the energy shift in Eq. (5.6) is then not very useful. The energy denominators also contain the energy shift, and an iterative solution must be used. However, the advantage of the Brillouin-Wigner perturbation theory over the Rayleigh-Schrödinger perturbation theory is its simpler structure. In order to convert the Brillouin-Wigner perturbation expansion into a Rayleigh-Schrödinger perturbation expansion, it is necessary to expand out the energy shift $\mathcal{E}_0 - E_0$ from the denominator. It can be absorbed into the interaction V, changing it to V'.[40]

An alternative to this clumsy procedure is to choose the arbitrary parameter E such that the unperturbed energy and true ground-state energy are equal,

$$E_0 = \mathcal{E}_0 . \tag{5.9}$$

Then the energy denominators in Eqs. (5.7) and (5.8) are automatically of the Rayleigh-Schrödinger type, and the energy shift is contained in the perturbation V.

In the expansion of the ground-state energy $\mathcal{E}_0$ there are some terms in which a single particle-hole pair occupies the intermediate state. A typical term in nth order is

$$\mathcal{E}_0^{(n)}(a,i) = \frac{\langle\Phi_0|V|\Phi_i^a\rangle\langle\Phi_i^a|V|\Phi_i^a\rangle}{D_i^a} \cdots \frac{\langle\Phi_i^a|V|\Phi_i^a\rangle\langle\Phi_i^a|V|\Phi_0\rangle}{D_i^a}, \tag{5.10}$$

where the perturbation potential V occurs n times.

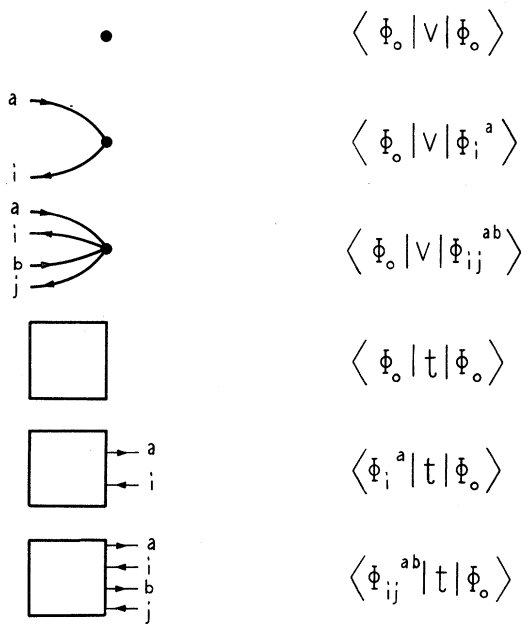

FIG. 6. The correspondence between the graphical quantities in Fig. 5 and the mathematical quantities in Eq. (5.6).

This term is expressed graphically in Fig. 7.

The term in Eq. (5.10) is potentially "dangerous," since for a poor choice of basis functions it may happen that

$$\left|\frac{\langle\Phi_i^a|V|\Phi_i^a\rangle}{D_i^a}\right| > 1 \tag{5.11}$$

when the states a and i are both near the Fermi surface, so the energy denominator is small. In this case the absolute value of Eq. (5.10) would be divergent as $n \to \infty$. Since the perturbation expansion is assumed to converge, the large contributions of the type shown in Eq. (5.10) and Fig. 7 would presumably have both positive and negative signs which would tend to cancel. However, from the numerical point of view, the difference between large quantities would lead to considerable uncertainty in the final result.

In order to prevent the term in Eq. (5.10) or Fig. 7 from contributing, the condition that the end vertices in Fig. 7 vanish can be imposed, which is from Fig. 6 just the Brillouin condition given in Fig. 2 and Eq. (2.12). The second term on the right in Fig. 5 and Eq. (5.6) for the ground-state energy will thus vanish for the HF orbitals.

However, the same term will also vanish if the Brillouin-Brueckner condition of Fig. 4 and Eq. (3.15) is imposed. Since the Brillouin condition is the simpler of the two, it would appear that no advantage would be gained by using the Brillouin-Brueckner condition. However, whole classes of additional diagrams, shown in Fig. 8, vanish if the Brillouin-Brueckner condition is used. The diagrams of Fig. 8 are potentially dangerous also, since it is possible to have a single particle-hole pair in an intermediate state which can scatter an infinite number of times.

The Brillouin condition results in only the *compensation of the lowest-order danger diagrams* (CLODD), whereas the Brillouin-Brueckner condition compensates all the potentially dangerous diagrams. This argument, when combined with the variational principles given previously, gives a strong case for determining the single-particle orbitals and potential such that the Brillouin-Brueckner condition is satisfied.[57]

VI. CONCLUSION

The results of this paper are summarized in Ta-

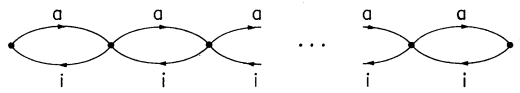

FIG. 7. A contribution to the ground-state energy in nth order in which there is only a single particle-hole pair in the intermediate state.

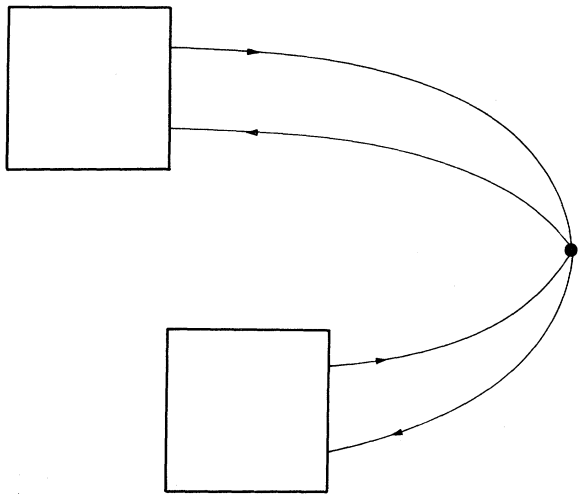

FIG. 8. A class of "dangerous" diagrams which will not contribute to the ground-state energy if the Brillouin-Brueckner condition is used.

ble I, which gives a comparison of the maximum-overlap orbitals with HF orbitals. The HF orbitals have the advantage over the maximum-overlap orbitals only in that the unperturbed ground-state energy is minimized. However, a comparison of Figs. 1 and 3 shows that the minimum of the unperturbed energy is always an upper bound to the true ground-state energy, whereas in the ESCF the minimum (or extremum) of an energy functional lies exactly on the true ground-state energy. Even though the Rayleigh-Ritz variational principle is not applicable to the ESCF, the occurrence of the minimum on the true ground-state energy has advantages if approximations are to be used. In particular, it is usually only the two-body part of the reaction operator t_2 that is calculated. If $t_2[\phi]$ is equal to the true reaction operator with a set of orbitals that differ only in first order $t[\phi+\delta\phi]$, the energy will be changed only in second order because of this stationary property.

Hartree-Fock theory is of course determined by the Brillouin condition in Eq. (2.12), whereas the maximum-overlap orbitals are determined by replacing V with t in Eq. (3.2), and calling the resulting Eq. (3.15) the Brillouin-Brueckner condition. If the Brillouin-Löwdin condition defined previously[20] for natural orbitals is expanded in perturbation theory, the first-order term in t is just the Brillouin-Brueckner condition. If both the Brillouin-Löwdin condition and the Brillouin-Brueckner condition are expanded in perturbation theory, the first-order term in V is just the Brillouin condition. From this point of view the maximum-overlap orbitals thus stand somewhere between the HF and the natural orbitals.[58]

The true Hamiltonian H in Eq. (2.1) is obviously independent of the choice of orbitals, so as an operator it cannot be varied. However, the "effective Hamiltonian" H_0+t does depend on the choice of orbitals, and can thus be varied as an operator. The condition obtained for its expectation value is completely equivalent to the Brillouin-Brueckner

TABLE I. A comparison of HF orbitals and maximum-overlap orbitals.

Properties	HF orbitals	Maximum-overlap orbitals
Ground-state energy	$H_{00}=\langle\Phi_0\|(H_0+V)\|\Phi_0\rangle$ = minimum [a]	$\mathcal{E}_0=\langle\Phi_0\|(H_0+t)\|\Phi_0\rangle$ = constant [b, c]
Diagonalization conditions	Brillouin condition [d] $\langle\Phi_0\|V\|\Phi_{se}\rangle=0$	Brillouin-Brueckner condition $\langle\Phi_0\|t\|\Phi_{se}\rangle=0$
Energy operators	$\langle\Phi_0\|\delta(H_0+V)\|\Phi_0\rangle\equiv 0$ [e, f]	$\langle\Phi_0\|\delta(H_0+t)\|\Phi_0\rangle=0$ [e]
Distance between Ψ [g] and Φ_0 $\|\|\Psi-\Phi_0\|\|$	Not minimum	Minimum
Overlap $\langle\Psi\|\Phi_0\rangle$	Not maximum	Maximum
Singly excited configurations in Ψ	Contribute in second order in V	Do not contribute
Dangerous diagrams	CLODD [h] (Fig. 2)	PCDD (I) (Fig. 4)

[a] Φ_0 is a Slater determinant in Eq. (2.8).
[b] $\mathcal{E}_0$ is the true ground-state energy in Eq. (3.1).
[c] t is the full reaction operator in Eq. (3.2).
[d] Φ_{se} is a singly excited configuration in Eq. (2.13).
[e] This expression denotes the expectation value of the variation of the operator with respect to the orbitals.
[f] The Hamiltonian is independent of the orbitals [cf. Eq. (2.1)].
[g] Ψ is the true ground-state wave function in Eq. (3.1).
[h] CLODD – compensation of lowest-order dangerous diagrams.

condition, as can be seen by varying Eq. (3.4) for $\mathcal{E}_0$, which gives zero identically.

The minimum distance in Hilbert space and the maximum overlap between the true and model wave functions are, of course, equivalent. They both imply that no singly excited configuration contributes to the true ground-state energy. However, because of the Brillouin condition in HF theory the *singly excited* configurations contribute only to second order in V. Møller and Plesset pointed out that for the single-particle density matrix in HF theory there are no first-order contributions in V to the perturbation expansion.[59]

The HF theory corresponds to the CLODD shown in Fig. 2, whereas the maximum-overlap orbitals correspond to the PCDD shown in Fig. 4. Natural orbitals were also shown to correspond to the PCDD, but to a different form. In order to distinguish these two forms, they can be referred to as the PCDD (I) and (II), respectively.

The HF orbitals have the advantage over the maximum overlap orbitals in that for potentials for which their equations exist, they are easier to calculate. The Brillouin-Brueckner condition must be imposed on the reaction operator calculated from the Lippmann-Schwinger equation in Eq. (3.5). However, since this is a sum of many-body operators, it is notoriously difficult to solve. Even in the two-body approximation, the solution is still difficult. However progress in solving the Lippmann-Schwinger equation in scattering theory has been made by Weinberg,[60] who points out some of the difficulties which would be encountered in considering the full many-body problem. His line of attack appears to be fruitful, and work in this direction is in progress. If only the two-body part of the reaction operator were retained, the result would be a self-consistent Brueckner-HF theory. If only the two- and three-body parts of the reaction operator were retained, the result would be a self-consistent Bethe-Faddeev-Brueckner-HF theory.[61]

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