Then the norms of $\mathbf{G}$ are defined by the following formulas:

$$\textit{Operator norm}:\ ||\mathbf{G}||_\infty = (\lambda_1)^{\frac{1}{2}}$$

$$\textit{Schmidt norm}:\ ||\mathbf{G}||_2 = \left\{\sum_{j=1}\lambda_j\right\}^{\frac{1}{2}},$$

$$\textit{Trace norm}:\ ||\mathbf{G}||_1 = \sum_{j=1}(\lambda_j)^{\frac{1}{2}}.$$

The inequalities used in this note are the following: For every kernel $\mathbf{G}$

$$|\text{trace } \mathbf{G}| \leqslant \text{trace norm } \mathbf{G}.$$

Given another kernel $\mathbf{F}(x;y)$, define the composite kernel

$$\mathbf{L}(x';x) = \int_y \mathbf{F}(x',y)\mathbf{G}(x,y)\ ;$$

then

$$||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_2||\mathbf{G}||_2$$

$$||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_\infty||\mathbf{G}||_1 \text{ and } ||\mathbf{L}||_1 \leqslant ||\mathbf{F}||_1||\mathbf{G}||_\infty.$$

The Schmidt norm is conveniently evaluated. In fact, it is easily seen that

$$\int_{x,x'}|\mathbf{G}(x;x')|^2 = \sum_{j=1}\lambda_j.$$

Moreover, for an arbitrary complete orthonormal system $\{\psi_j\}$, the following (Schmidt's theorem) is valid

$$\sum_{j=1}\int_x\left|\int_{x'}\mathbf{G}(x';x)\psi_j(x')\right|^2 = \int_{x,x'}|\mathbf{G}(x';x)|^2.$$

This can be proved by expanding $\mathbf{G}(x';x)$, as a function of x', in terms of $\{\psi_j(x')\}$ and then applying the Parseval relation.

7. Wielandt's Inequality

Given two $N \times N$ Hermitian matrices $\mathbf{A}$ and $\mathbf{B}$ with eigenvalues $\{\lambda_j\}$ and $\{\mu_j\}$ in non-increasing order, respectively, Wielandt's theorem[25] reads

$$\sum_{j=1}^{N}|\lambda_j-\mu_j| \leqslant \sum_{j=1}^{N}|\rho_j|,$$

where $\{\rho_j\}$ are the eigenvalues of $\mathbf{A}-\mathbf{B}$. This can be modified for the integral kernels.

Let $\mathbf{F}$ and $\mathbf{G}$ be two nonnegative definite kernels with the eigenvalues $\{\lambda_j\}$ and $\{\mu_j\}$, respectively; then

$$\sum_{j=1}|\lambda_j-\mu_j| \leqslant \text{trace norm } (\mathbf{F}-\mathbf{G}).$$

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The author would like to thank Professor Harrison Shull for his encouragement during helpful discussions. He also wishes to express his appreciation for the hospitality of the quantum chemistry group at Indiana University.

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[25] H. Wielandt, Proc. Am. Math. Soc. 6, 106 (1955).

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Wave and Reaction Operators in the Quantum Theory of Many-Particle Systems*

PER-OLOV LÖWDIN

Quantum Theory Project, University of Florida, Gainesville, Florida and

Quantum Chemistry Group, Uppsala University, Uppsala, Sweden

1. INTRODUCTION

THE basic problem in the current quantum theory of matter is the solution of the many-particle problem connected with the Schrödinger equation $\mathcal{H}\Psi = E\Psi$ for the stationary states. For atomic, molecular, and solid-state systems, the problem is simple in the sense that the Hamiltonian is assumed to be at least approximately known, whereas for nucleonic systems the interaction potentials are still not determined. Here we concentrate essentially on the general features of many-particle systems having a Hamiltonian of the form:

$$\mathcal{H}_{\text{op}} = \sum_i \mathcal{H}_i + \sum_{i<j}\mathcal{H}_{ij} + \sum_{i<j<k}\mathcal{H}_{ijk} + \cdots. \quad (1)$$

In the theoretical interpretation of the experimental data for electronic systems, the so-called "in-

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dependent-particle model" has been remarkably successful. The idea goes back to Bohr,[1] and it was further developed for atoms by Hartree[2] in his famous SCF calculations. In this model, each electron moves in the field of the nucleus (or nuclei) and the average field of all other electrons corresponding to a certain "effective" Hamiltonian. This intuitive idea was brought in connection with the many-electron Schrödinger equation through the work by Slater[3] and Fock,[4] who showed that one could derive one-electron wave equations of the type

$$\mathcal{H}_{\text{eff}}\psi_k = \epsilon_k\psi_k , \tag{2}$$

by approximating the total wave function Ψ by a product of one-electron functions $\psi_1, \psi_2, \cdots, \psi_N$ and applying the variation principle. If the Pauli principle is taken into account through the antisymmetry requirement, the total wave function is instead approximated by a single determinant built up from the spin orbitals $\psi_1, \psi_2, \cdots, \psi_N$. This approach has been very successful in the applications to various electronic systems. In atomic theory, it meets us under the name of the Hartree–Fock scheme[5]; in molecular theory, it is characterized by the symbol ASP–MO–LCAO–SCF[6]; and, in solid-state physics, it forms the basis for the band theory of conductors, semiconductors, and insulators.[7]

The energy error in the independent particle model based on a single Slater determinant is usually called the "correlation error," and, for a discussion of its character and order of magnitude, we will refer elsewhere.[8] Here it is sufficient to mention a typical case: the correlation energy for the hydrogen molecule is -1.06 eV, which actually consists of two contributions 1.06 eV and -2.12 eV associated with the correlation errors in the kinetic energy and Coulomb interactions, respectively, according to the virial theorem. Since 1 eV = 23.07 kcal/mole, these errors are certainly of essential importance. In considering various aspects of the Hartree–Fock scheme, one can easily distinguish between the optimists and the pessimists: the optimists claim that, since the correlation error is hardly one percent of the total energy, the relative accuracy is high and the over-all picture good, whereas the pessimists emphasize that most physicists and chemists are usually not interested in total energies but actually in "energy differences" which are small in comparison to the correlation energies.

The qualitative success of the Hartree–Fock scheme to describe the occurrence of closed structures in atoms, molecules, and solid state was usually attributed to the fact that the electrons interact so weakly through the Coulomb forces that the electrons move practically independent of each other. It was hence somewhat of a surprise, when Goeppert-Mayer[9] and Jensen[10] discovered that the independent particle approximation was just as useful in nuclear theory in connection with the famous nuclear shell model. Since the nucleons interact very strongly, one had now to look for a new explanation of the success of the one particle schemes, and Brueckner[11] pointed out that two-body correlations could actually be incorporated in the self-consistent-field schemes, if one replaced "interactions" with "reactions" in the derivation of the effective potentials. This procedure is discussed further below.

In order to reach beyond the Hartree–Fock scheme, one has to achieve greater accuracy in solving the Schrödinger equation and, in this work, Professor Egil Hylleraas has been the great pioneer. In his papers[12] on the helium atom, he has established the basic methods and principles that have been leading the development up to date. He emphasized the importance of the proper choice of coordinates as well as the proper choice of basis in Hilbert space; he stressed the fact that the discrete hydrogen-like functions do not form a complete set, and that one has to include the continuum or modify the character of the set to make it complete. Here I mention three of Hylleraas's methods that have been of particular importance, since they have been generalized to many-

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[1] N. Bohr, Proc. Phys. Soc. (London) **35**, 296 (1923).

[2] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).

[3] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[4] V. Fock, Z. Physik **61**, 126 (1930).

[5] Atomic SCF calculations have been reviewed in a series of papers; see, e.g., D. R. Hartree, *Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957); D. R. Hartree, Repts. Prog. Phys. **11**, 113 (1948); P.-O. Löwdin. Proc. Robert A. Welch Foundation Conf. Chem. Res. II, Atomic Structure **1958**, 5.

[6] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); P.-O. Löwdin, Phys. Rev. **97**, 1490 (1955).

[7] For a survey, see, e.g., P.-O. Löwdin, J. Appl. Phys. **33**, 251 (1962).

[8] P.-O. Löwdin, *Advances in Chemical Physics,* edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 207.

[9] M. Goeppert-Mayer, Phys. Rev. **74**, 235 (1948); **75**, 1969 (1949); **78**, 16, 22 (1950).

[10] M. E. Mayer and J. H. D. Jensen, *Nuclear Shell Theory* (John Wiley & Sons, Inc., New York, 1955).

[11] K. A. Brueckner, C. A. Levinson, and H. M. Mahmoud, Phys. Rev. **95**, 217 (1954); K. A. Brueckner, Phys. Rev. **96**, 508 (1954); **97**, 1353 (1955); **100**, 36 (1955); K. A. Brueckner and C. A. Levinson, Phys. Rev. **97**, 1344 (1955); H. A. Bethe, Phys. Rev. **103**, 1353 (1956); J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957); H. A. Bethe and J. Goldstone, Proc. Roy. Soc. (London) **A238**, 551 (1957); L. S. Rodberg, Ann. Phys. **2**, 199 (1957); to mention only a selection of the rich literature on this subject.

[12] E. A. Hylleraas, Z. Physik **48**, 469 (1928); **54**, 347 (1930); **65**, 209 (1930); and several other papers; see E. A. Hylleraas, "Abhandlungen aus den Jahren 1926–37" (Oslo, 1956).

electron systems: namely; (a) the split-orbital method, (b) the method using a correlation factor containing the interparticle distances r_{ij}, and (c) the method of superposition of configurations. The first approach has led to the general method of using "different orbitals for different spins" that has been discussed in detail at another session of this symposium. The second one represents the simplest way of applying Hylleraas's idea of "correlated wave functions" to a many-particle system, whereas the last method is essentially an application of the Ritz's expansion method to the Schrödinger equation.

The purpose of this paper is to show the interrelation between the three methods and the modern treatment of the many-particle problem based on the concepts of wave and reaction operators. Usually, these concepts are derived from infinite-order perturbation theory, but here they are derived by means of an elementary partitioning technique.[13] The results are also used to discuss the exact self-consistent-field theory[14] mentioned above. It is hoped that the discussion gives some idea of the mathematical and conceptual structure of several of the methods used in treating many-particle systems and their internal relationships.

2. WAVE AND REACTION OPERATORS

Let us consider a Hamiltonian $\mathcal{H} = \mathcal{H}_0 + V$, where V is a perturbation which is not necessarily small, and let φ_0 be a normalized eigenfunction to $\mathcal{H}_0$ associated with the eigenvalue E_0, so that

$$\mathcal{H}_0\varphi_0 = E_0\varphi_0\,, \quad \langle\varphi_0|\varphi_0\rangle = 1\,. \tag{3}$$

Note that we start out from a *single* unperturbed eigenfunction, which is not yet further specified. In order to find a solution Ψ to the Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{4}$$

we now introduce a *wave operator* W, which is defined through the relations

$$\Psi = W\varphi_0\,, \quad \langle\Psi|\varphi_0\rangle = 1\,. \tag{5}$$

The wave operator hence changes the unperturbed eigenfunction into the perturbed one, and the normalization is chosen so that Ψ is the sum of φ_0 and a term orthogonal to φ_0. The solution can later easily be renormalized.

Multiplying the eigenvalue equation (4) to the left by φ_0^* and integrating, we obtain

$$\langle\varphi_0|\mathcal{H}|\Psi\rangle = E\langle\varphi_0|\Psi\rangle = E$$

and further

$$\begin{aligned} E &= E_0 + \langle\varphi_0|V|\Psi\rangle \\ &= E_0 + \langle\varphi_0|VW|\varphi_0\rangle\,. \end{aligned} \tag{6}$$

It is hence convenient to introduce the *reaction operator* t through the relation

$$t = VW\,, \tag{7}$$

since the expectation value of this operator with respect to φ_0 then gives the exact energy shift:

$$E = E_0 + \langle\varphi_0|t|\varphi_0\rangle\,. \tag{8}$$

In order to derive formal expressions for W and t, we now introduce the projection operator O connected with the unperturbed eigenfunction φ_0:

$$O = |\varphi_0\rangle\langle\varphi_0| = \varphi_0\langle\varphi_0| \tag{9}$$

and its *orthogonal complement* $P = 1 - O$. One has the relations:

$$O^2 = O\,, \quad O^+ = O\,, \quad \mathrm{Tr}\,(O) = 1\,, \tag{10}$$

$$P^2 = P\,, \quad P^+ = P\,, \quad OP = PO = 0\,, \tag{11}$$

$$P\varphi_0 = 0\,. \tag{12}$$

For the projection of an arbitrary function Φ, one has $O\Phi = \varphi_0\langle\varphi_0|\Phi\rangle$ and particularly $O\Psi = \varphi_0$ according to (5). Since $(\mathcal{H} - E)\Psi = 0$, one has the following identity:

$$\begin{aligned} \Psi &= (O + P)\Psi = \varphi_0 + PK^{-1}K\Psi \\ &= \varphi_0 + PK^{-1}[K + P(\mathcal{H} - E)(O + P)]\Psi \\ &= \varphi_0 + PK^{-1}P\mathcal{H}\varphi_0 \\ &\qquad + PK^{-1}[K - P(E - \mathcal{H})P]\Psi\,. \end{aligned} \tag{13}$$

Here K is an arbitrary nonsingular operator at our disposal, and we now try to use it to get rid of the last term. It is tempting to put $K = P(E - \mathcal{H})P$, but this is actually not possible, since this operator is singular and has no inverse. Instead, we put

$$K = \alpha O + P(E - \mathcal{H})P\,, \quad T = PK^{-1}P\,, \tag{14}$$

where α is an arbitrary number different from zero. Since $OK^{-1}P = PK^{-1}O = 0$, the last term in (13) still disappears, and we obtain

$$\Psi = \varphi_0 + TV\varphi_0 = (1 + TV)\varphi_0\,, \tag{15}$$

i. e.,

$$W = 1 + TV\,. \tag{16}$$

Hence, we have obtained a formal expression for the wave operator containing the operator T, which is characterized by the relations

$$OT = TO = 0\,, \quad P(E - \mathcal{H})T = P\,. \tag{17}$$

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[13] P.-O. Löwdin, J. Math. Phys. **3**, 969 (1962); for numerical aspects, see J. Mol. Spectr. **10**, 12 (1963).

[14] P.-O. Löwdin, J. Math. Phys. **3**, 1171 (1962).

Since $\partial T/\partial \alpha = -PK^{-1}OK^{-1}P = 0$, the operator T is independent of α. In the following, for historic reasons, we use the symbolic notation

$$T = P/(E - \mathcal{H}) \tag{18}$$

but remember that it corresponds to the full definition of (14) with $\alpha \neq 0$. In summary, we have the relations

$$W = 1 + TV\,, \quad t = V + VTV\,, \tag{19}$$

which form the basis of the theory. By means of (18) and (8), one obtains further

$$t = V + V\frac{P}{(E_0 - \mathcal{H}_0) - (V - \langle\varphi_0|t|\varphi_0\rangle)}V\,, \tag{20}$$

which is the fundamental expression for the evaluation of the reaction operator. It may be used to construct first- and second-order iteration procedures to evaluate $\langle\varphi_0|t|\varphi_0\rangle$, and we note particularly the connection between the Newton–Raphson formula and the variation principle treated elsewhere.[14] The wave operator is obtained afterwards by leaving out the left-hand factor V, and for the true normalization integral, one gets finally

$$\langle\Psi|\Psi\rangle = \langle\varphi_0|1 + VT^2V|\varphi_0\rangle\,.$$

Connection with Infinite-Order Perturbation Theory

If the inverse operator occurring in the definition (14) of T is evaluated by means of a power series expansion of the type

$$\begin{aligned}(A - B)^{-1} &= A^{-1} + A^{-1}B(A - B)^{-1}\\ &= A^{-1} + A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} + \cdots\,, \end{aligned}\tag{21}$$

one gets formulas corresponding to various types of perturbation theory. There are two essential partitionings to be discussed:

$$E - \mathcal{H} = (E - \mathcal{H}_0) - V \tag{22}$$

$$= (E_0 - \mathcal{H}_0) - (V - \langle t\rangle_0)\,, \tag{23}$$

and the first one is said to be of Brillouin type and the second one of Schrödinger type. Introducing the notations

$$T_0 = P/(E - \mathcal{H}_0)\,, \quad R_0 = P/(E_0 - \mathcal{H}_0)\,, \tag{24}$$

we obtain the expansions:

$$\begin{aligned}T &= T_0\sum_{k=0}^{\infty}(VT_0)^k\\ &= R_0\sum_{k=0}^{\infty}[(V - \langle\varphi_0|t|\varphi_0\rangle)R_0]^k\,,\end{aligned}\tag{25}$$

from which one easily derives the standard Brillouin and Schrödinger perturbation series.[14] For a simple treatment of the so-called linked-cluster theorem in the latter, we refer to a previously published paper.[15]

3. SOME ASPECTS ON THE ONE-PARTICLE SCHEME

So far, we have not emphasized the many-particle aspects of the eigenvalue problem (4), and we note that the formal expressions (19) and (20) are valid for all types of Hamiltonians. Starting out from (1), we write

$$\mathcal{H}_0 = \textstyle\sum_i (\mathcal{H}_i + u_i)\,, \tag{26}$$

$$V = -\sum_i u_i + \sum_{i<j}\mathcal{H}_{ij} + \sum_{i<j<k}\mathcal{H}_{ijk} + \cdots\,, \tag{27}$$

where the potentials u_i are at our disposal. The unperturbed problem (3) is now separable and has the solution

$$\varphi_0 = \prod_{i=1}^{N}\psi_i\,, \qquad E_0 = \prod_{i=1}^{N}\epsilon_i\,, \tag{28}$$

$$(\mathcal{H}_i + u_i)\psi_i = \epsilon_i\psi_i\,, \tag{29}$$

where $(\mathcal{H}_i + u_i)$ may be considered as an effective Hamiltonian for the particle i. The relation $\Psi = W\varphi_0$ implies that the exact solution may be obtained by letting the wave operator work on a Hartree product φ_0, which is often characterized as a "model" function. Various approximate solutions can now be obtained by choosing different approximate forms for the wave operator.

Correlation-Factor Approach

One way to proceed is to approximate the operator W by a multiplicative factor g, which is then analogous to Hylleraas's "correlation factor." Usually one assumes that g has the form:

$$g = g(r_{12}, r_{13}, r_{23}, \cdots) \tag{30}$$

and is a symmetric function of all the interparticle distances r_{ij} involved. The good results obtained on the helium atom[16] and on the hydrogen molecule[17] by means of simple correlation factors are very promising. It is interesting to note that, in the Bohm–Pines[18] plasma model for the solid state, the collective oscillations corresponding to the correlation effects enter

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[15] See reference 14, p. 1179.

[16] P.-O. Löwdin and L. Redei, Phys. Rev. **114**, 752 (1959).

[17] A. A. Frost, J. Braunstein, and W. Schwemer, J. Am. Chem. Soc. **70**, 3292 (1948); W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 205 (1960).

[18] See, e.g., D. Pines, Solid State Phys. **1**, 368 (1957).

into such a correlation factor, and that the total wavefunction is approximated by the form $\Psi \approx g\varphi_0$. Wigner's[19] study of the electronic correlation in the alkali metals is somewhat different, but Krisement[20] has pointed out that his wavefunction is still close to the form $g\varphi_0$.

In conclusion, it should be observed that the theory developed by Dalgarno and Lewis[21] putting $W = 1 + F$ belongs essentially to the same category.

Projection Operator Approach

Let us now look at the case when there is a normal constant of motion Λ which commutes with the Hamiltonian (1) and has the eigenvalues $\lambda_1, \lambda_2, \cdots, \lambda_n$. The eigenfunction Ψ to $\mathcal{H}$ is then also an eigenfunction to Λ or (in the case of a degenerate level E) may be chosen that way. Since Λ commutes with $\mathcal{H}_0$ only for very special choices of the potentials u_i, the unperturbed function φ_0 is usually not an eigenfunction to Λ, and it is then an essential feature of the wave operator W to restore this property. It is often convenient to approximate the wave operator by a projection operator

$$O_k = \prod_{l \neq k} \frac{\Lambda - \lambda_l}{\lambda_k - \lambda_l}, \tag{31}$$

which selects the proper component associated with the eigenvalue λ_k out of φ_0. A constant factor is further needed to give the proper normalization according to (5).

Symmetry properties of $\mathcal{H}$ are treated similarly by means of the group-theoretical projection operators. The total wavefunction is hence approximated by a $\Lambda-$ or symmetry projection of a Hartree product, and this approach leads to the extended Hartree–Fock scheme discussed in greater detail at another session of this symposium. Since it contains the method using "different orbitals for different spins" as a special case, it is closely related to the split-orbital method introduced by Hylleraas.

It should finally be observed that the wave operator can be approximated by a product of a correlation factor g and a projection operator O, and that wave functions of the form $gO\varphi_0$ with proper choices of φ_0 and g may have excellent accuracy.[22]

Superposition of Configurations

Let us extend the set of one-particle functions $\psi_1, \psi_2, \cdots, \psi_N$ with another set $\psi_{N+1}, \psi_{N+2}, \cdots$ orthogonal to the former so that the resulting set is mathematically complete. By forming all possible products of N factors out of this set, we obtain a basis $\varphi_0, \varphi_1, \varphi_2, \cdots$, which spans the N-particle Hilbert space completely, and it is then easy to express P in terms of these functions. The application of the wave operator (14) to φ_0 leads then to an infinite expansion in terms of the set $\{\varphi_k\}$ corresponding to a superposition of configurations, where the coefficients are determined by the properties of the wave operator. Hence, there is a close connection between the results obtained by using infinite-order perturbation theory, the wave operator, or an infinite-order secular equation. The approach based on "second quantization" can also be conveniently studied from this point of view; so many different approaches can hence be given a common basis. With this remark we conclude the study of the three fundamental methods given by Hylleraas and their relation to modern theory.

4. EXACT SELF-CONSISTENT-FIELD METHOD

The classical Hartree scheme was based on the variation principle $\delta\langle\varphi_0|\mathcal{H}_0 + V|\varphi_0\rangle = 0$, where φ_0 was a Hartree product of the type given in (28). The resulting effective Hamiltonians $(\mathcal{H}_i + u_i)$ contain Hartree potentials u_i given by the formula:

$$u_i = \sum_j \langle\psi_j|\mathcal{H}_{ij}|\psi_j\rangle + \sum_{j<k} \langle\psi_j\psi_k|\mathcal{H}_{ijk}|\psi_j\psi_k\rangle + \cdots, \tag{32}$$

where the summations go over all indices $\neq i$, and the self-consistent-field (SCF) calculations are then based on the cycle

$$\{\psi_i\} \rightarrow u_i \rightarrow \mathcal{H}_{\mathrm{eff}} \rightarrow \{\psi_i\}\ . \tag{33}$$

In addition to the original Hartree product $\varphi_0 = \psi_1\psi_2\cdots\psi_k\cdots\psi_N$, we now consider a "singly excited product"

$$\varphi_{\mathrm{s.e.}} = \psi_1\psi_2\cdots\bar{\psi}_k\cdots\psi_N\ , \tag{34}$$

where one of the original orbitals ψ_k has been replaced by an "excited" orbital $\bar{\psi}_k$ orthogonal to ψ_k, so that $\langle\bar{\psi}_k|\psi_k\rangle = 0$. The definition (27) of the perturbation potential V leads then to the identity:

$$\langle\varphi_{\mathrm{s.e.}}|V|\varphi_0\rangle = 0\ , \tag{35}$$

which is known as Brillouin's theorem.[23] Sometimes, it is also written in the form $\langle\varphi_{\mathrm{s.e.}}|\mathcal{H}|\varphi_0\rangle = 0$, but it should be observed that this theorem does not prevent singly excited terms to occur in the expansion

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[19] E. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

[20] O. Krisement, Phil. Mag. **2**, 245 (1957).

[21] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1955); Proc. Phys. Soc. (London) **A69**, 628 (1956).

[22] P.-O. Löwdin, Rev. Mod. Phys. **32**, 328 (1960).

[23] L. Brillouin, Actualités Sci. Ind. No. 71 (1933); No. 159 (1934); C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

of the exact expansion of the eigenfunction Ψ. In the literature, there are certainly some misunderstandings about this point into the Hartree scheme: the singly excited terms should always be properly investigated and included, and it is completely erroneous to think that the expectation values of one-particle operators $\Omega = \sum_i \Omega_i$ will be given with higher relative accuracy than the total energy—usually the reverse will be true. For the kinetic energy $T = \sum_i P_i^2/2m$, the error is actually the same as in the total energy (but with the opposite sign, depending on the virial theorem).

According to (6), one has the exact formula $E = E_0 + \langle\varphi_0|V|\Psi\rangle$. It has been observed by Nesbet[24] and Sinanoğlu[25] that, for Hamiltonians which contain two-particle interactions $\mathcal{H}_{ij}$ but no many-particle interactions, one obtains

$$\begin{aligned} E &= E_0 + \langle\varphi_0|V|\varphi_0\rangle + \langle\varphi_0|V|\Psi_{\mathrm{d.e.}}\rangle \\ &= \langle\varphi_0|\mathcal{H}|\varphi_0\rangle + \langle\varphi_0|\sum_{i<j}\mathcal{H}_{ij}|\Psi_{\mathrm{d.e.}}\rangle\,, \end{aligned} \tag{36}$$

where $\Psi_{\mathrm{d.e.}}$ is the sum of all terms in Ψ which are "doubly excited" with respect to φ_0. The last term represents the "correlation energy," which hence depends only on φ_0 and the doubly excited term in the expansion of Ψ subject to the normalization $\langle\Psi|\varphi_0\rangle = 1$. Sinanoğlu[25] has taken this observation as the basis for his interesting approach emphasizing the fact that $\Psi_{\mathrm{d.e.}}$ may be written in terms of φ_0 and a set of "pair functions." Again, I feel that the importance of accumulated effect of the singly excited, the triply excited, and more highly excited terms in Ψ should not be underestimated in treating general correlation effects.

These remarks are here made in connection with the Hartree scheme, but it should be observed that the corresponding theorems hold in the same form in the Hartree–Fock scheme, if φ_0 is given as a Slater determinant and the interactions $\mathcal{H}_{ij}, \mathcal{H}_{ijk}\cdots$ in (32) are replaced by the operators

$$\bar{\mathcal{H}}_{ij} = \mathcal{H}_{ij}(1 - P_{ij}) \tag{37}$$

$$\bar{\mathcal{H}}_{ijk} = \mathcal{H}_{ijk}(1 - P_{ij} - P_{ik} - P_{jk} + P_{ijk} + P_{ikj})\,, \tag{38}$$

where the P's are permutation operators.

Let us now return to the problem of the singly excited terms which has been given an interesting treatment in Brueckner's theory.[11] As mentioned in the introduction, Brueckner wanted to generalize the SCF theory in such a way that it would take even strong two-body interactions into full account, and here we proceed still further and suggest an exact formulation of the SCF method.[14] The Hartree scheme is based on the variation principle $\langle\mathcal{H}\rangle = \langle\varphi_0|\mathcal{H}_0 + V|\varphi_0\rangle$, giving an upper bound to the true energy, whereas the *exact SCF method* is based on the exact formula (8) of the form $E = \langle\varphi_0|\mathcal{H}_0 + t|\varphi_0\rangle$, indicating that one obtains the exact energy, if one replaces the perturbation V by the reaction t, i. e.,

$$V \longrightarrow t \tag{39}$$

$$\begin{aligned} -\sum_i u_i + \sum_{i<j}\mathcal{H}_{ij} + \sum_{i<j<k}\mathcal{H}_{ijk} + \cdots \rightarrow -\sum_i u_i \\ + \sum_{i<j} t_{ij} + \sum_{i<j<k} t_{ijk} + \cdots\,. \end{aligned} \tag{40}$$

In the expansion of t, Brueckner included the two-body reactions t_{ij} but neglected the higher terms. Here, all the terms in t are fully included in the formal treatment. If t is momentarily fixed, and the expression $\langle\varphi_0|\mathcal{H}_0 + t|\varphi_0\rangle$ is minimized, one obtains one-particle Schrödinger equations of the type (2) or (29), where the potentials u_i are given by formula (32) with the interactions $\mathcal{H}_{ij}, \mathcal{H}_{ijk}, \cdots$ replaced by the reactions $t_{ij}, t_{ijk}, \cdots$:

$$u_i = \sum_j \langle\psi_j|t_{ij}|\psi_j\rangle + \sum_{j<k}\langle\psi_j\psi_k|t_{ijk}|\psi_j\psi_k\rangle + \cdots\,, \tag{41}$$

where the summations go over all indices $\neq i$. This definition leads immediately to the identity

$$\langle\varphi_{\mathrm{s.e.}}|t|\varphi_0\rangle = 0\,, \tag{42}$$

which is the so-called "Brillouin–Brueckner theorem." One can then show that, if the expansion of Ψ is based on the one-particle functions $\psi_1, \psi_2, \cdots, \psi_N$ in φ_0 and their orthogonal complement, the *singly excited terms vanish identically*. The goal of the more elementary theories can hence be fully reached in the exact SCF theory. For further details, we refer to another paper.[14]

Symmetry Properties in the Exact SCF Theory

It has been realized long ago that the symmetry properties of a physical many-particle system play an important role in the treatment of the correlation problem. In the exact SCF scheme, the role of the reaction operator is stressed, but one should be careful not to overemphasize this aspect of the problem on behalf of the symmetry properties. We have here discussed the extension of the Hartree scheme, but it is well known that, for fermions, the introduction of the antisymmetry requirement reduces the orig-

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[24] R. K. Nesbet, Communication at the Summer Institute on Quantum Chemistry, Uppsala, 1960 (unpublished).

[25] O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 376 (1961); J. Chem. Phys. **36**, 706, 3198 (1962).

inal "correlation energy" by approximately a factor one half and focuses the interest on particles of opposite spins. In the Hartree–Fock scheme, the remaining correlation error in the energy can be further reduced, say about 85%, by introducing "different orbitals for different spins" and by studying the component of proper symmetry uniquely defined by the basic Slater determinant. Hence, it is apparent that by the combination of symmetry considerations and Hylleraas's split-orbital idea, one can remove about 90% of the original correlation error in the energy, before one has to introduce the concept of the reaction operator.

It is easy, in principle, to combine the basic ideas in the two approaches involving symmetry and reactions. If the total Hamiltonian $\mathcal{H}$ has a normal constant of motion Λ, so that $\mathcal{H}\Lambda = \Lambda\mathcal{H}$, it is well known that an eigenfunction Ψ to $\mathcal{H}$ is also an eigenfunction to Λ or (in the case of a degenerate energy level) may be chosen in that way. It is now convenient to divide the many-particle Hilbert space into subspaces associated with the eigenvalues $\lambda_1, \lambda_2, \cdots, \lambda_n$ to Λ, for instance by means of the projection operators O_k defined by (31). These subspaces are orthogonal and noninteracting with respect to $\mathcal{H}$ and Λ, so that they are essentially independent of each other. The unperturbed wavefunction φ_0 may now be chosen as the O_k projection of the Slater determinant built up from the N one-particle functions $\psi_1, \psi_2, \cdots, \psi_N$; this defines the projection operator $O = |\varphi_0\rangle\langle\varphi_0|$, and it is then sufficient to introduce the orthogonal complement P with respect to the subspace associated with the eigenvalue λ_k alone in investigating the "reaction." This means an essential simplification, and our study gives an idea how a synthesis of many of the current ideas for treating many-particle systems can ultimately be achieved.

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Discussion on Perturbation Theory and Reaction Operators

O. Sinanoğlu, *Chairman*

Nesbet: Despite the great amount of theoretical work on the many-particle perturbation theory, especially following the work of Brueckner and Goldstone, there have been very few applications to finite systems. The implicit claim of this theory is that one can get reliable results by abandoning variational methods in favor of selective summation of Feynman diagrams in the perturbation theory. Obviously this is a quantitative issue; to resolve it, we must have detailed computations. One of the first serious efforts to apply this theory to an electronic system (the ground state of Be) has just been completed by Hugh P. Kelly, in his Ph.D. dissertation, 1962 (unpublished) at the University of California, Berkeley, supervised by Professor K. M. Watson. Kelly has computed the continuum eigenfunctions of the Be Hartree–Fock operator, and has integrated over the continuum in evaluating Feynman–Goldstone diagrams. One interesting result is that he finds it essential to use the complete diagonal energy difference in energy denominators, for example, for single excitation,

$$\mathcal{E}_a - \mathcal{E}_b - (ab|R|ab) \,, \tag{1}$$

rather than the formula characteristic of the second quantization approach

$$\mathcal{E}_a - \mathcal{E}_b \,, \tag{2}$$

changing from Eq. (2) to Eq. (1) involves a summation of diagrams to infinite order. Quantum chemists will, of course, recognize Eq. (1) as the natural energy denominator to use, since it is just the difference between energy mean values of the two interacting Slater determinants [see, e.g., R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955)]. It was found that important contributions to the energy come from diagrams different from the ladder diagrams considered in the Brueckner theory. Kelly gets 2.48 eV for the correlation energy of Be, compared with R.