PHYSICAL REVIEW VOLUME 147, NUMBER 4 29 JULY 1966

N-Representability Problem for Fermion Density Matrices. II. The First-Order Density Matrix with N Even[*]

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(Received 19 August 1965)

For a quantum-mechanical system of N identical fermions, the N-representability problem is the problem of recognizing whether, for a given pth-order reduced density matrix $\Gamma^{(p)}(12\cdots p|1'2'\cdots p')$, there exists an antisymmetric N-particle wave function $\Psi(12\cdots N)$ such that $\Gamma^{(p)}(12\cdots p|1'2'\cdots p')=\binom{N}{p}\int\Psi(12\cdots N)\times\Psi^*(1'2'\cdots p',\,p+1\cdots N)d\tau_{p+1}\cdots d\tau_N$. It is shown that if the Hamiltonian of a system is time-reversal invariant, and the number of particles, N, is even, the necessary and sufficient condition that an approximate first-order density matrix corresponding to a nondegenerate energy eigenstate be N-representable is that its natural spin-orbital occupation numbers be equal in pairs.

The quantum-mechanical expectation value of any p-particle operator depends only on the pth-order (reduced) density matrix $\Gamma^{(p)}$. For example, if the wave function $\Psi(x_1x_2\cdots x_n)\equiv\Psi(12\cdots N)$ is known, $\Gamma^{(p)}$ is defined by

$$\Gamma^{(p)}(12\cdots p|1'2'\cdots p')=\binom{N}{p}\int\Psi(12\cdots p,p+1\cdots N)\times\Psi^*(1'2'\cdots p',p+1\cdots N)d\tau_{p+1}\cdots d\tau_N\,,\quad(1)$$

and the expectation value of, say, a Hamiltonian of the form $\mathcal{H}_{\text{op}}=\sum_i H_i+\sum_{i<j}H_{ij}$ is given in terms of the second-order density matrix by[1]

$$\langle\mathcal{H}_{\text{op}}\rangle_{\text{av}}=\int\left[\frac{2}{N-1}H_1+H_{12}\right]\Gamma^{(2)}(12|1'2')d\tau_1d\tau_2.$$

Here x_i represents the space and spin coordinates of the particle i. For the case of fermions (bosons), a given density matrix $\Gamma^{(p)}$ is said to be N-representable if there exists an antisymmetric (symmetric) wave function Ψ in terms of which the given $\Gamma^{(p)}$ can be represented according to (1). The importance of the N-representability problem (the problem of recognizing when a $\Gamma^{(p)}$ is N-representable) is that if $\Gamma^{(p)}$ could be varied over the set of N-representable pth-order density matrices, one could replace the energy-variation method for the wave function by an energy-variation method for the density matrix. Thus, the N-body problem could be reduced to a two-body problem for a Hamiltonian of the form of the above example.

In a previous paper[1] the N-representability problem was solved for the second-order density matrix for $N=3$ fermions. Here, we shall be concerned with the first-order fermion density matrix for N even. Then (1) becomes, with $\Gamma^{(1)}\equiv\gamma$

$$\gamma(1|1')=N\int\Psi(12\cdots N)\Psi^*(1'2\cdots N)d\tau_2\cdots d\tau_N.\quad(1')$$

In the case of atomic and molecular systems with fixed nuclei, the diagonal elements $\gamma(1|1)$ characterize the electronic charge distribution, and the full matrix $\gamma(1|1')$ enables one to calculate the expectation value of any one-particle operator $A=\sum_i A_i$,

$$\langle A\rangle=\int A_1\gamma(1|1')d\tau_1,\quad(2)$$

where A_1 works only on the unprimed coordinate, and the prime is then removed before the integration. For the electronic Hamiltonian with fixed nuclei,

$$\mathcal{H}=\sum_i(T_i+V_i)+\sum_{i<j}V_{ij}\,,$$

one needs the second-order density matrix in general for energy expectation values, but one can calculate the total electronic energy of an eigenstate from an exact knowledge of $\gamma(1|1')$ alone, since the virial theorem requires $E=-T$, and the kinetic energy T can be calculated by (2). Although we have no way at present of finding the exact γ without a knowledge of the exact Ψ, it is nevertheless of interest to study the conditions that a physically realizable γ must satisfy, that is, the N-representability conditions for γ.

The known conditions[2,3] for the N-representability of a first-order density matrix are

A. γ must be Hermitian, $\gamma(1|1')=\gamma^*(1'|1)$,

B. γ must be positive semidefinite,

$$\int\varphi(1)\gamma(1|1')\varphi^*(1')d\tau_1d\tau_{1'}\geqslant0$$

for any normalizable one-particle function φ,

C. γ must have finite trace. We shall assume here that γ is normalized to N:

$$\text{Tr}\gamma=\int\gamma(1|1)d\tau_1=N,$$

D. The eigenvalues n_i of γ must satisfy $n_i\leqslant1$.

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[*] Abstracted from Report 54 of the Quantum Theory Project, University of Florida, Gainesville, Florida, 1964, by D. W. Smith. Supported in part by Grant No. GP 1695 from the National Science Foundation and in part by Grant No. NsG-512 from the National Aeronautics and Space Administration.

[1] D. W. Smith, J. Chem. Phys. 43, S258 (1965).

[2] A. J. Coleman, Can. Math. Bull. 4, 209 (1961); Rev. Mod. Phys. 35, 668 (1963).

[3] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

If N is even and the Hamiltonian is time-reversal invariant, these conditions enable us to give the necessary and sufficient conditions that a trial first-order density matrix for a nondegenerate energy eigenstate be N-representable. We stated and proved the following theorem elsewhere[4] but with the normalization $\mathrm{Tr}\gamma = 1$. In the present normalization, $\mathrm{Tr}\gamma = N$, we restate

Theorem 1: A sufficient condition for the N-representability of a first-order density matrix γ is that it satisfy conditions A to D and that all eigenvalues of γ be evenly degenerate (have multiplicities divisible by two).

First-order density matrices with doubly degenerate eigenvalues occur widely in physics and chemistry. For example, if Ψ is an eigenfunction to S_z, then the natural spin-orbitals can be chosen to have pure α or pure β spin functions. (A simple proof of this assertion is given by Löwdin.[5]) The first-order density matrix will then be of the form

$$\gamma(1|1') = \gamma^+(r_1|r_1')\alpha(\zeta_1)\alpha^*(\zeta_1') + \gamma^-(r_1|r_1')\beta(\zeta_1)\beta^*(\zeta_1'), \quad (3)$$

where r_1 represents the spatial coordinates of particle 1, and ζ_1 its spin coordinate. If the eigenvalue of S_z is zero, then, since $\gamma^+ = \gamma^-$, each eigenvalue will be doubly degenerate.[6]

Micha[7] showed that even when spin-orbit coupling is taken into account in atomic wave functions, and Ψ is no longer an eigenfunction of S_z, this double degeneracy will still arise if Ψ is an eigenfunction of J_z and of the time-reversal operator.

We can show that this double degeneracy is actually much more general.

Theorem 2: If the Hamiltonian of a system is invariant under time reversal, then the natural spin-orbitals associated with any nondegenerate energy eigenstate have their occupation numbers equal in pairs.

Before proving Theorem 2, we shall prove three lemmas.

The time-reversal operator K appropriate for this problem is, in the standard representation for spin functions,[8]

$$K = e^{i\pi S_y/\hbar} K_0 = Y_1 Y_2 \cdots Y_N K_0, \quad (4)$$

where K_0 is complex conjugation ($K_0\Psi = \Psi^*$), $S_y = \sum_{i=1}^{N} s_{yi}$ is the y-component of the spin angular-momentum operator, and $Y_j = e^{i\pi s_{yj}/\hbar}$. Now K is an antiunitary operator,[8] that is, it is unitary ($KK^\dagger = 1$) and antilinear:

$$K(c_1\Psi_1 + c_2\Psi_2) = c_1^* K\Psi_1 + c_2^* K\Psi_2. \quad (5)$$

Further $K^2 = +1$ if N is even, and $K^2 = -1$ if N is odd. Any antilinear operator can be written as the product of K_0 and a linear operator, and it is only K_0 in (4) which is antilinear.

The "turnover rule" for a linear operator F,

$$\int \Psi_1^* F \Psi_2 d\tau = \int (F^\dagger \Psi_1)^* \Psi_2 d\tau,$$

becomes, for an antilinear operator K,

$$\int \Psi_1^* K \Psi_2 d\tau = \int (K^\dagger \Psi_1) \Psi_2^* d\tau. \quad (6)$$

By hypothesis, $\mathcal{H}$ commutes with K. This commutation is assumed to hold for all quantum-mechanical systems as long as no external magnetic fields are present. Therefore, we have

Lemma 1: If Ψ is an energy eigenfunction ($\mathcal{H}\Psi = E\Psi$) and $\mathcal{H}K = K\mathcal{H}$ then $K\Psi$ is also an energy eigenfunction with the same eigenvalue

$$\mathcal{H}(K\Psi) = K(\mathcal{H}\Psi) = E(K\Psi).$$

If Ψ is nondegenerate, $K\Psi$ can differ from Ψ only by a phase factor:

$$K\Psi = e^{i\alpha}\Psi. \quad (7)$$

The antilinear property of K enables us to choose the phase of Ψ such that $\Psi' = e^{i\beta}\Psi$ belongs to the eigenvalue $+1$ of K. For if $\beta = \alpha/2$,

$$K\Psi' = Ke^{i\alpha/2}\Psi = e^{-i\alpha/2}K\Psi = e^{i\alpha/2}\Psi = \Psi'.$$

Lemma 2: If under the hypothesis of Lemma 1, Ψ is nondegenerate, the number of electrons N must be even. (This is a consequence of Kramers' theorem.)

Proof: If N is odd, $K^2 = -1$, $K = -K^\dagger$, and $K\Psi$ is orthogonal to Ψ:

$$\int \Psi^* K\Psi d\tau = \int (K^\dagger\Psi)\Psi^* d\tau = -\int (K\Psi)\Psi^* d\tau = 0, \quad (8)$$

where we have used (6). Since Ψ and $K\Psi$ are orthogonal eigenfunctions belonging to the same energy eigenvalue E, this eigenvalue cannot be nondegenerate, contrary to hypothesis. Therefore, N must be even if Ψ is nondegenerate.

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[4] D. W. Smith, Rev. Mod. Phys. 35, 688 (1963).

[5] P. O. Löwdin, Rev. Mod. Phys. 35, 629 (1963).

[6] See, for example, R. McWeeny, Rev. Mod. Phys. 32, 335 (1960).

[7] D. A. Micha, Uppsala Quantum Chemistry Group Report No. 99, 1963 (unpublished). See also J. Chem. Phys. 41, 3648 (1964).

[8] E. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959), Chap. 26; see also A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. II, Chap. 15.

Lemma 3: If under the hypothesis of Lemma 1, Ψ is nondegenerate,

$$[K_1,\gamma]=0\,, \tag{9}$$

where $K_1 \equiv K_0 \exp(i\pi s_{y1}/h) \equiv K_0 Y_1$ is the one-particle time-reversal operator and γ is the integral operator whose kernel is γ. (For electrons, we have $Y_1 = i\sigma_{y1}$, where σ_{y1} is a Pauli spin operator.)

Proof: We wish to show that

$$K_1\gamma u(1)=\gamma K_1 u(1) \tag{10}$$

for every function $u(1)$ in the domain of γ. Since by hypothesis, Ψ is a nondegenerate energy eigenfunction, its phase can be chosen such that $K\Psi=\Psi$, with $K=Y_1Y_2\cdots Y_NK_0$. Then we have

$$\begin{aligned}
K_1\gamma u(1) &= K_1\int \gamma(1\,|\,1')u(1')d\tau_{1'} \\
&= K_1 N\int \Psi(12\cdots N)\Psi^*(1'2\cdots N)u(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= N\int Y_1\Psi^*(12\cdots N)\Psi(1'2\cdots N)u^*(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= N\int [Y_2^\dagger\cdots Y_N^\dagger Y_1\cdots Y_N K_0\Psi(12\cdots N)]\Psi(1'2\cdots N)u^*(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= N\int \Psi(12\cdots N)[Y_2\cdots Y_N\Psi^*(1'2\cdots N)]^*u^*(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= N\int \Psi(12\cdots N)[Y_{1'}^\dagger Y_{1'}Y_2\cdots Y_N K_0\Psi(1'2\cdots N)]^*u^*(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= N\int \Psi(12\cdots N)\Psi^*(1'2\cdots N)Y_{1'}u^*(1')d\tau_{1'}d\tau_2\cdots d\tau_N \\
&= \int \gamma(1\,|\,1')K_{1'}u(1')d\tau_{1'} = \gamma K_1 u(1)\,,
\end{aligned} \tag{11}$$

where we have used the fact that Y_1 is linear, and the K_0 implicit in K_1 acts on everything to its right in (10). We have also used the fact that $K_0Y_j = Y_jK_0$ since Y_j is real, and that $[Y_i,Y_j]=0$ since these operators operate on separate variables if $i\neq j$.

We may now prove Theorem 2: Since $K_1\gamma=\gamma K_1$, $K_1f_i(1)$ is a natural spin-orbital (an eigenfunction of γ) if $f_i(1)$ is. But $K_1f_i(1)$ according to (18) is orthogonal to $f_i(1)$ and must therefore be another natural spin orbital having the same eigenvalue (occupation number) as $f_i(1)$.

Thus the N-representability problem for the first-order density matrix γ for nondegenerate (exact or trial) energy eigenfunctions is solved for systems having Hamiltonians invariant under time reversal. Such energy eigenfunctions must have an even number of electrons, otherwise they would have a Kramers degeneracy. We need only impose the double degeneracy on the eigenvalues of γ, since this condition is both necessary and sufficient to ensure N-representability by a nondegenerate (exact or approximate) energy eigenfunction.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor P. O. Löwdin and Professor A. J. Coleman for stimulating discussions concerning this problem. He also wishes to thank Professor Kimio Ohno, Dr. J. L. Calais, and Oswaldo Goscinski for helpful criticism of the manuscript. Finally, he wishes to acknowledge with gratitude the financial support of the National Science Foundation and the National Aeronautics and Space Administration.