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Density Matrix and the Many-Body Problem

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The application of the two-particle density matrix to the calculation of approximate ground states for many-body systems is discussed. It is shown that the subsidiary conditions employed by Mayer in this context are insufficient to ensure that a valid result is obtained. The formulation of adequate subsidiary conditions presents considerable difficulty.

INTRODUCTION

THE suggestion has been made by Löwdin¹ and Mayer² that the problem of finding an approximation to the ground state of a many-body system might be approached with advantage by employing the density matrix. They both point out that the energy levels of systems involving only two-body forces are completely characterized by the two-particle density matrix. Thus the energy may be expressed in terms of the density matrix element and the variational procedure applied to obtain the ground state.

Mayer² has actually carried through this procedure for the case of a gas of electrons immersed in a uniform positive charge. The further discussion of the use of the density matrix will, in this paper, be confined to this particular case. This is because Mayer's methods afford a concrete example for discussion and also because this particular model affords the only true many-body problem having a simple exact solution in the Hartree-Fock approximation. A comparison with the Hartree-Fock solution will be important in the subsequent discussion. Mayer's method (which will be discussed in more detail below) depends on finding a simple trial form for the two-particle density matrix element which has the required symmetry and which reduces properly to the one-particle element on the application of the appropriate operations. The energy is then expressed in terms of this element and minimized, the process being subject to the appropriate normalization condi-

tions. All the relevant physical information is thus apparently included. The results are, however, rather surprising. Mayer finds that there is a minimum distance of approach for pairs of electrons beyond which the probability density is zero. This is in complete disagreement with the results of various problems involving small numbers of electrons which have been studied in detail by other methods. These include the classical works of Hylleraas³ and the problem of two electrons moving in a "three-dimensional linear oscillator potential" which may be solved exactly.⁴ These cases indicate that the probability density goes to zero at $r=0$ for the triplet case and remains finite at $r=0$ for the singlet case. Thus, for a large assembly of electrons, one would expect the mean probability density to be small but finite at $r=0$. This is in marked contrast with Mayer's² result.

Now these disagreements with existing results could possibly be explained in terms of the particular trial form assumed for the density matrix element or attributed to a qualitative difference between the cases of very few and very many electrons. However, by using the framework of Mayer's² method and applying his subsidiary conditions, it is possible to obtain certain entirely absurd results. It is the purpose of this paper to point this out and to show that the problem is rather more complex than has been assumed. Thus, though this method offers great possibilities, it requires modification before becoming a practicable method of

¹ P. O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).

² J. E. Mayer, *Phys. Rev.* **100**, 1579 (1955).

³ E. A. Hylleraas, *Z. Physik* **48**, 469 (1928); **54**, 347 (1929); **65**, 209 (1930).

⁴ R. H. Tregold and J. S. Evans (to be published).

calculation. In order to discuss the question further, it is necessary to recapitulate certain of the relevant portions of Mayer's² paper. This is done in the next section.

OUTLINE OF MAYER'S METHOD

An assembly of N electrons in a box of volume V is considered. The density is then

$$\rho_0 = (N/V) \text{ electrons per cc.} \quad (1)$$

The box is supposed to contain a uniform positive charge of density $e\rho_0$. The unit of length is chosen to be $\rho_0^{-1/3}$ and the unit of energy is the atomic unit = 27.21 ev. c is the concentration of electrons per cubic Bohr radius. The Hamiltonian is then

$$H = -\frac{1}{2}c^3 \sum_{i=1}^N \nabla_i^2 + c^3 \left\{ \sum_{N \geq i \geq j \geq 1} \frac{1}{x_{ij}} - \sum_{i=1}^N \int_{x_{i0}}^1 \frac{1}{x_{i0}} d^3x_0 + \frac{1}{2} \int_{x_{01}}^1 \frac{1}{x_{01}} d^3x_0 d^3x_1 \right\}. \quad (2)$$

Let ψ be the complete wave function for the system and q_i the combined space-spin set of coordinates for the i th electron. The two-particle density matrix element is defined as

$$\begin{aligned} \rho_{2\sigma}(\mathbf{q}_1', \mathbf{q}_1''; \mathbf{q}_2', \mathbf{q}_2'') \\ \equiv N(N-1) \int \cdots \int \psi^*(\mathbf{q}_1', \mathbf{q}_2', \mathbf{q}_3, \cdots, \mathbf{q}_N) \\ \times \psi(\mathbf{q}_1, \mathbf{q}_2'', \mathbf{q}_3, \cdots, \mathbf{q}_N) dq_3 \cdots dq_N, \end{aligned} \quad (3)$$

and the matrix element for the coordinates of position alone is

$$\rho_2(\mathbf{x}_1', \mathbf{x}_1''; \mathbf{x}_2', \mathbf{x}_2'') = \int \int \rho_{2\sigma} d\sigma_1 d\sigma_2, \quad (4)$$

where the σ 's denote the spin coordinates. The single-particle density matrix element is defined as

$$\rho_1(\mathbf{x}_1', \mathbf{x}_1'') = \frac{1}{N-1} \int \rho_2(\mathbf{x}_1', \mathbf{x}_1''; \mathbf{x}_2, \mathbf{x}_2) d^3x_2. \quad (5)$$

The functions $f(x)$ and $g(x)$ are defined as

$$f(x) = \rho_1(\mathbf{x}', \mathbf{x}''), \quad x = |\mathbf{x}' - \mathbf{x}''|, \quad (6)$$

$$1 - g(x_{12}) = \rho_2(\mathbf{x}_1, \mathbf{x}_1; \mathbf{x}_2, \mathbf{x}_2). \quad (7)$$

It may then be shown that

$$\frac{E}{N} = -\frac{3}{2}c^3 \left[\frac{d^2 f(x)}{dx^2} \right]_{x=0} - \frac{1}{2}c^3 \int_0^\infty 4\pi x g(x) dx. \quad (8)$$

It is further shown in Mayer's² paper that the appropriate symmetry conditions can be satisfied and the two-particle matrix element can be made to reduce to the one-particle element properly if

$$g(x) = \frac{1}{2}f^2(x) + [1 - \frac{1}{2}f^2(x)][2k(x) - k^2(x)], \quad (9)$$

where $f(x)$ and $k(x)$ are even real functions of x . These functions are now chosen to minimize the energy as given by (8), subject to the two conditions

$$\int_0^\infty 4\pi x^2 g(x) dx = 1 \quad (10)$$

and

$$0 \leq \phi(t) \leq 2, \quad (11)$$

where

$$\phi(t) = \int_0^\infty 4\pi x^2 f(x) \frac{\sin 2\pi x t}{2\pi x t} dx. \quad (12)$$

The first of these conditions expresses the normalization of the total wave function and the second, the fact that not more than two electrons of opposite spins can occupy one state. A full explanation of why this should be cannot be given here and reference must be made to the original source (Mayer²) for the derivation of these results.

DISCUSSION OF MAYER'S METHOD²

As will be seen from (8), the function $k(x)$ does not appear in the expression for the kinetic energy and therefore can be chosen to minimize the potential energy subject only to the condition (10).

However, if the form of the function $f(x)$ corresponding to the Hartree-Fock solution is denoted by $f_0(x)$, it can be shown that

$$\int_0^\infty 4\pi x^2 \frac{1}{2} f_0^2(x) dx = 1, \quad (13)$$

and thus, according to Mayer,² Eq. (10) may be satisfied for nonzero $k(x)$ only if $f(x)$ differs from $f_0(x)$. Thus the introduction of correlation implies $k(x) \neq 0$ for certain values of x and this in turn implies an increase of kinetic energy over the Hartree-Fock value. This would, of course, be expected. It is thus found that

$$\begin{aligned} k(x) &= 1, & 0 \leq x \leq x_0, \\ k(x) &= 0, & x_0 < x \leq \infty, \end{aligned} \quad (14)$$

where x_0 is a parameter subsequently determined by variational means.

However, it is important to notice that if $k(x)$ is allowed to assume negative values over part of the region $x > x_0$, it is obviously possible to choose a form

such that

$$\int_0^{\infty} 4\pi x [1 - \frac{1}{2} f^2(x)] [2k(x) - k^2(x)] dx > 0 \quad (15)$$

and

$$\int_0^{\infty} 4\pi x^2 g(x) = 1, \quad (16)$$

with $f(x) = f_0(x)$.

Now if (15) and (16) can be simultaneously satisfied, the implication is that the potential energy has been lowered as compared with the Hartree-Fock solution. However, $f(x) = f_0(x)$ implies that the occupation of states in momentum space remains the same as in the Hartree-Fock treatment. If this result is considered from the standpoint of configuration interaction, it is seen to be in error since there is only one possible configuration corresponding to $f_0(x)$. Thus if $k(x)$ is

allowed to take on negative values, the method breaks down. However, there appears to be no physical or mathematical reason why $k(x)$ should not take on negative values over part of the range of x . It is not even surprising if this behavior makes $g(x)$ negative for certain regions of x since such behavior is physically allowable.

CONCLUSIONS

It thus appears that the methods discussed in this paper cannot be employed with confidence unless some other set of auxiliary conditions can be introduced to ensure that the two-particle density matrix can be derived from an allowable wave function.

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