

Hierarchy equations for reduced density matrices*

Leon Cohen[†]

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514

C. Frishberg

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

(Received 20 October 1975)

Starting with Schrödinger's time-independent equation for N indistinguishable particles, an exact equation is derived for the reduced density matrix of order s , ρ_s . The equation contains terms dependent on ρ_{s+1} and ρ_{s+2} . The Hartree-Fock equation is derived, without recourse to the variational method, by assuming that ρ_2 and ρ_3 are particular functionals of ρ_1 .

I. INTRODUCTION

The important physical quantities in the study of atoms and molecules can be obtained from the low-order reduced density matrices. Schrödinger's equation is an equation for the full density matrix, and hence, even if it could be solved, the solution contains much more information than is necessary. This situation is analogous to statistical mechanics where Liouville's equation is an equation for the distribution function of all the particles in the system, but nonetheless it is only the low-order distribution functions which are of particular interest.

A very fruitful approach in classical statistical mechanics is the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy.¹ The basic idea is to start with Liouville's equation for the N -body distribution and integrate out $N-s$ of the particles, thus obtaining an equation for the reduced distribution function of order s . The equation obtained is not self-contained in that it has terms depending on the higher-order distribution. The entire set of hierarchy equations are still exact. To proceed

further one must decouple the hierarchy. Depending on the physical situation, this is accomplished by approximating the higher-order distribution as a functional of the lower-order distribution. The resulting equation, or set of equations, is thus self-contained and in principle can be solved.

Our intent in this paper is to develop a similar procedure for the time-independent Schrödinger equation. In Sec. II we derive the hierarchy equation for reduced density matrices. In Sec. III we obtain the Hartree-Fock equation, without the use of the variational method, by making a particular functional approximation on the second- and third-order reduced density matrices in terms of the first-order density matrix. The functional assumption made is that of no correlations between particles but with antisymmetry imposed.

The notation we shall use is as follows: The full density matrix for a system containing N indistinguishable particles is defined as

$$\rho_N(x_1, x_2, \dots, x_N; x'_1, x'_2, \dots, x'_N) = \psi(x_1, \dots, x_N)\psi^*(x'_1, \dots, x'_N). \quad (1.1)$$

The reduced density matrix of order s is

$$\rho_s(x_1, \dots, x_s; x'_1, \dots, x'_s) = \binom{N}{s} \int \rho_N(x_1, \dots, x_s, x_{s+1}, \dots, x_N; x'_1, \dots, x'_s, x'_{s+1}, \dots, x'_N) dx_{s+1}, \dots, dx_N. \quad (1.2)$$

We shall restrict ourselves to Hamiltonians which are of the form

$$H_N = \sum_{i=1}^N \Omega_i + \sum_{ij} \Omega_{ij}, \quad (1.3)$$

where Ω_i are one-body operators and Ω_{ij} are two-body multiplicative operators.

Quantities of the form

$$\int \Omega_s \rho(x_1, \dots, x_s, \dots; x'_1, \dots, x'_s, \dots) dx_s \quad (1.4)$$

shall be taken to mean that one first operates on the unprimed variables with Ω_s and then sets $x_s = x'_s$ before the integration.

II. HIERARCHY EQUATIONS

Starting with the Schrödinger time-independent equation for N indistinguishable particles,

$$H_N \rho_N = E \rho_N, \quad (2.1)$$

we integrate out x_{s+1}, \dots, x_N ,

$$\int H_N \rho_N dx_{s+1}, \dots, dx_N = E \binom{N}{s}^{-1} \rho_s. \quad (2.2)$$

For the part of the Hamiltonian which consists of the one-body interactions we have

$$\sum_{i=1}^N \int \Omega_i \rho_N dx_{s+1}, \dots, dx_N = \binom{N}{s}^{-1} \sum_{i=1}^s \Omega_i \rho_s + \binom{N}{s+1}^{-1} (N-s) \int \Omega_{s+1} \rho_{s+1} dx_{s+1}. \quad (2.3)$$

We divide the two-body interaction part as follows:

$$\begin{aligned} \sum_{ij}^N \int \Omega_{ij} \rho_N dx_{s+1}, \dots, dx_N &= \binom{N}{s}^{-1} \sum_{ij}^s \Omega_{ij} \rho_s + \sum_{\substack{i \leq s \\ j > s}} \int \Omega_{ij} \rho_N dx_{s+1}, \dots, dx_N + \sum_{\substack{i > s \\ j > s}} \int \Omega_{ij} \rho_N dx_{s+1}, \dots, dx_N \\ &= \binom{N}{s}^{-1} \sum_{ij}^s \Omega_{ij} \rho_s + \binom{N}{s+1}^{-1} (N-s) \sum_{i=1}^s \int \Omega_{i,s+1} \rho_{s+1} dx_{s+1} \\ &\quad + \binom{N}{s+2}^{-1} \frac{(N-s)(N-s-1)}{2} \int \Omega_{s+1,s+2} \rho_{s+2} dx_{s+1} dx_{s+2}. \end{aligned} \quad (2.4)$$

$$\quad (2.5)$$

If we define the reduced Hamiltonian by

$$H_s = \sum_{i=1}^s \Omega_i + \sum_{ij}^s \Omega_{ij}, \quad H_1 = \Omega_1, \quad (2.6)$$

and combine Eqs. (2.2), (2.3), and (2.5), we have the hierarchy equations for reduced density matrices for the time-independent case,

$$\begin{aligned} H_s \rho_s + (s+1) \int \left(\Omega_{s+1} + \sum_{i=1}^s \Omega_{i,s+1} \right) \rho_{s+1} dx_{s+1} \\ + \frac{1}{2} (s+2)(s+1) \int \Omega_{s+1,s+2} \rho_{s+2} dx_{s+1} dx_{s+2} = E \rho_s. \end{aligned} \quad (2.7)$$

For the special case of $s=N-1$, the third term of the left-hand side of Eq. (2.7) is absent.

Specializing to the case $s=1$ gives

$$H_1 \rho_1 + 2 \int (\Omega_2 + \Omega_{12}) \rho_2 dx_2 + 3 \int \Omega_{23} \rho_3 dx_2 dx_3 = E \rho_1. \quad (2.8)$$

Equations (2.7) and (2.8) are exact equations. To proceed further one must decouple them at some stage in the hierarchy. That is, one must express ρ_{s+1} and ρ_{s+2} as functionals of ρ_s in some approximation.

We remark that we could have started equally well with the complex-conjugate Hamiltonian operating on the primed variables and obtained the identical equation (2.7) except that the operators would be complex conjugated and would operate on the primed variables. If we assume the operators are real, then by subtraction we have

$$\begin{aligned} (H_s - H'_s) \rho_s \\ + (s+1) \int \left((\Omega_{s+1} - \Omega'_{s+1}) + \sum_{i=1}^s (\Omega_{i,s+1} - \Omega'_{i,s+1}) \right) \\ \times \rho_{s+1} dx_{s+1} = 0 \end{aligned} \quad (2.9)$$

For the time-dependent case the left-hand side of Eq. (2.9) is equated to $i\hbar(\partial\rho_s/\partial t)$.

III. HARTREE-FOCK EQUATION

A natural first attempt at breaking the chain of equations given by Eq. (2.7) is to assume the particles are uncorrelated and that the second- and third-order density matrices are factorable into first-order density matrices,

$$\rho_2(x_1, x_2; x'_1, x'_2) = \rho_1(x_1; x'_1) \rho_1(x_2; x'_2), \quad (3.1)$$

$$\rho_3(x_1, x_2, x_3; x'_1, x'_2, x'_3) = \rho_1(x_1; x'_1) \rho_1(x_2; x'_2) \rho_1(x_3; x'_3). \quad (3.2)$$

If Eqs. (3.1) and (3.2) are inserted into (2.8), one then obtains the Hartree equation for indistinguishable particles. But of greater interest is the case of fermions where we antisymmetrize (3.1) and (3.2) to obtain

$$\rho_2(x_1, x_2; x'_1, x'_2) = \frac{1}{2} \begin{vmatrix} \rho_1(x_1; x'_1) & \rho_1(x_1; x'_2) \\ \rho_1(x_2; x'_1) & \rho_1(x_2; x'_2) \end{vmatrix}, \quad (3.3)$$

$$\rho_3(x_1x_2x_3; x'_1x'_2x'_3) = \frac{1}{3!} \begin{vmatrix} \rho_1(x_1; x'_1) & \rho_1(x_1; x'_2) & \rho_1(x_1; x'_3) \\ \rho_1(x_2; x'_1) & \rho_1(x_2; x'_2) & \rho_1(x_2; x'_3) \\ \rho_1(x_3; x'_1) & \rho_1(x_3; x'_2) & \rho_1(x_3; x'_3) \end{vmatrix}. \quad (3.4)$$

These forms for ρ_2 and ρ_3 also arise from a single determinant wave function.²

We shall show that the above functional assumption on ρ_2 and ρ_3 leads to the Hartree-Fock equations when inserted into Eq. (2.8). We note that the variational method is not used. This is in

$$\begin{aligned} H_1\varphi_i(x_1) + \left(\sum_{k=1}^N \int \varphi_k^*(x_2)\Omega_{12}\varphi_k(x_2) dx_2 \right) \varphi_i(x_1) - \sum_{k=1}^N \left(\int \varphi_k^*(x_2)\Omega_{12}\varphi_i(x_2) dx_2 \right) \varphi_k(x_1) + \sum_{k=1}^N \langle k|\Omega|k\rangle\varphi_i(x_1) \\ - \sum_{k=1}^N \langle k|\Omega|i\rangle\varphi_k(x_1) + \frac{1}{2}\varphi_i(x_1) \left(\sum_{lk}^N \langle lk|\Omega_{12}|lk\rangle - \langle lk|\Omega_{12}|kl\rangle \right) - \sum_{lk}^N \varphi_i(x_1) \langle lk|\Omega_{12}|ik\rangle - \langle lk|\Omega_{12}|ki\rangle = E\varphi_i(x_1), \end{aligned} \quad (3.6)$$

where

$$\langle i|\Omega|k\rangle = \int \varphi_i^*(x)\Omega\varphi_k(x) dx, \quad (3.7)$$

$$\begin{aligned} \langle ij|\Omega_{12}|kl\rangle = \int \int \varphi_i^*(x_1)\varphi_j^*(x_2)\Omega_{12} \\ \times \varphi_k(x_1)\varphi_l(x_2) dx_1 dx_2. \end{aligned} \quad (3.8)$$

The first three terms of Eq. (3.6) are recognized to be the Hartree-Fock Hamiltonian F operating on $\varphi_i(x_1)$. Now, the total energy of system can be expressed exactly in terms of ρ_1 and ρ_2 ,

$$E = \int \Omega_1\rho_1 dx_1 + \int \Omega_{12}\rho_2 dx_1 dx_2, \quad (3.9)$$

and upon substituting Eqs. (3.3) and (3.4) into Eq. (3.9) we have

$$E = \sum_k \langle k|\Omega|k\rangle + \sum_{l < k} \langle lk|\Omega_{12}|lk\rangle - \langle lk|\Omega_{12}|kl\rangle, \quad (3.10)$$

which is the Hartree-Fock energy. Using this expression for E and defining

$$\epsilon_{ik} = \langle k|\Omega|i\rangle + \sum_l \langle kl|\Omega_{12}|il\rangle - \langle kl|\Omega_{12}|li\rangle, \quad (3.11)$$

contrast to the conventional approach of minimizing the energy, either with respect to the orbitals or the density matrix.³

Relating ρ_2 to ρ_1 by Eq. (3.3) implies that ρ_1 is idempotent and can therefore be expanded as²

$$\rho_1(x_1; x'_1) = \sum_{i=1}^N \varphi_i(x_1)\varphi_i^*(x'_1), \quad (3.5)$$

where the φ_i 's are the natural orbitals.

We now insert Eqs. (3.3) and (3.4) into Eq. (2.8). Multiplying by $\varphi_i(x_1)$ and integrating over dx_1 we obtain

Eq. (3.6) simplifies to

$$F\varphi_i(x) = \sum_k \epsilon_{ik}\varphi_k(x), \quad (3.12)$$

which is the Hartree-Fock equation. The appropriate unitary transformation to the canonical orbitals brings Eq. (3.12) to the usual diagonal form.

IV. CONCLUSION

That the Hartree-Fock equation follows naturally from the assumption of no correlations is analogous to the classical situation where one obtains the Vlasov equation¹ (collisionless Boltzmann equation). In both cases the physical interpretation is that a given particle is influenced by the smoothed-out potential of the others. Also, in both cases the smoothed-out potential has to be determined self-consistently. The approximation is particularly good when the force is long range as is the case with the Coulomb force.

There are a number of standard techniques which can be used to decouple the hierarchy and obtain equations which go beyond the correlationless case. For example, a cluster expansion of the density matrix should prove particularly useful. This and other possibilities are currently being investigated.

ACKNOWLEDGMENT

We thank Professor R. G. Parr for helpful discussions relating to this work.

*Aided by a research grant to the University of North Carolina from the National Science Foundation.

†Permanent address: Hunter College of the City University of New York, New York, N. Y. 10021. Work done during tenure of a grant from the City University

Faculty Research Award Program.

¹See, e.g., R. L. Liboff, *Introduction to the Theory of Kinetic Equations* (Wiley, New York, 1969).

²P. O. Löwdin, *Phys. Rev.* 97, 1474 (1955).

³R. McWeeny, *Rev. Mod. Phys.* 32, 355 (1960).