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VARIATIONAL CALCULATIONS WITH DENSITY MATRICES

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VARIATIONAL CALCULATIONS WITH
DENSITY MATRICES

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Introduction.

This paper will contain a brief review of the variational method developed by J. K. Percus and myself (1, 2) along with a description of some applications of the method which are presently in progress. In order to explain our notation and normalization we define the 1-matrix and the 2-matrix as follows:

$$\gamma(x|y) = \langle \Phi | \psi^\dagger(x) \psi(y) | \Phi \rangle$$

$$\Gamma(x_1, x_2 | y_1, y_2) = \langle \Phi | \psi^\dagger(x_2) \psi^\dagger(x_1) \psi(y_1) \psi(y_2) | \Phi \rangle$$

where ψ and $\psi^\dagger$ are boson (or fermion) field operators. In our analysis we have

utilized the obvious fact that, for any operator B, the expectation value $\langle \Phi | BB^\dagger | \Phi \rangle$ is non-negative. If we choose an operator B of the form:

$$B = C + \int b(x, y) \psi^\dagger(x) \psi(y) dx dy$$

then the fact that $\langle \Phi | BB^\dagger | \Phi \rangle$ is non-negative regardless of the value of the constant C and the function $b(x, y)$ leads fairly simply to the following necessary condition involving the 1-matrix and the 2-matrix:

$G(x_1, x_2 | y_1, y_2)$ has nonnegative eigenvalues, where:

$$G(x_1, x_2 | y_1, y_2) = \pm \Gamma(y_1, x_2 | x_1, y_2) + \delta(x_1 - y_1) \gamma(x_2 | y_2) - \gamma(x_1 | x_2) \gamma^*(y_1 | y_2).$$

The plus sign is taken if the particles are bosons while the minus sign is taken for fermions.

While the above condition is not sufficient to guarantee that γ and Γ are acceptable density matrices* the imposition of this condition, along with the more well-known restrictions (such as symmetry conditions on Γ and the non-negativity of the eigenvalues of γ and Γ) has been enough to yield exact results in the cases in which the variational calculation has been carried out exactly. These calculations are shown in Ref. 1.

Atoms and Molecules.

When the number of particles in the system is not very large it is reasonable

*See reference 1 for necessary and sufficient conditions.

to work in a truncated, finite-dimensional Hilbert Space. The matrices γ , Γ , and G then become finite-dimensional square matrices. In this case the task of performing a numerical minimization of the energy, expressed in terms of γ and Γ , while maintaining all the above-mentioned restrictions is difficult but not forbidding.

Suppose we consider the case of an N-electron atom. We expand all relevant functions in terms of a set of one-electron orbitals $\phi_n(r, \sigma)$, cutting off the expansions at $n=M$. Of course $M \gg N$. Looked upon as a purely numerical problem our task is then to minimize the quantity:

$$E = \sum H(n_1, n_2 | m_1, m_2) \Gamma(n_1, n_2 | m_1, m_2)$$

with the following constraints:

$$1. \Gamma(n_1, n_2 | m_1, m_2) = \Gamma^*(m_1, m_2 | n_1, n_2)$$

$$2. \Gamma(n_1, n_2 | m_1, m_2) = -\Gamma(n_2, n_1 | m_1, m_2)$$

$$3. \Gamma \text{ has no negative eigenvalues.}$$

$$4. \sum \Gamma(n, m | n, m) = N(N-1)$$

$$5. G(n_1, n_2 | m_1, m_2) \text{ has no negative eigenvalues, where}$$

$$G(n_1, n_2 | m_1, m_2) = -\Gamma(m_1, n_2 | n_1, m_2) + \delta_{n_1, m_1} \delta(n_2 | m_2) - \delta(n_1 | n_2) \delta^*(m_1 | m_2)$$

$$\text{and: } \gamma(n_1 | m_1) = \frac{1}{N-1} \sum \Gamma(n_1, n_2 | m_1, n_2).$$

The first four restrictions can be satisfied quite easily by writing in the form: $\Gamma(n_1, n_2 | m_1, m_2) = \beta \sum_{j=1}^{M^2} [C_j(n_1, n_2) - C_j(n_2, n_1)] [C_j^*(m_1, m_2) - C_j^*(m_2, m_1)]$

where the constants $C_j(n_1, n_2)$ are completely free while β is chosen to satisfy restriction 4.

It is the fifth restriction that makes the problem non-trivial. The author has been unable to find any way of handling this constraint except the obvious and time-consuming one of repeatedly checking the lowest eigenvalue of G . A program which will do the minimization in just that way is presently being prepared at Davis. The program will first be applied to the Berrilium atom. In that way it will be possible

to check our results with the recent calculations of ρ for Berrilium. (3, 4) It should be mentioned that the reason the Exclusion Principle is not added as a separate restriction is that it is included in restriction 5.

Translation-Invariant Systems.

For systems, such as nuclei or quantum fluids, which are described by translation-invariant Hamiltonians some simplifications can be made in the density matrix variational problem. (2) One first makes use of the fact that, within the space of translation-invariant wave functions, the eigenvalues and eigenfunctions of the operator $H + \alpha (\sum \nabla_j)^2$ are identical with those of the operator H . This allows the energy expectation value to be written in the form:

$$E = V \int \delta(\underline{r} - \underline{r}') \left[-\frac{\hbar^2}{16mN} \nabla_r^2 + \frac{1}{2} v(r) \right] \omega(\underline{r}, \underline{r}') d^3r d^3r'$$

where V is the system volume, $v(r)$ is the interparticle potential, and $\omega(\underline{r}, \underline{r}')$ is related to the 2-matrix in the following way:

$$\omega(\underline{r}, \underline{r}') = \rho(\frac{1}{2}\underline{r}, -\frac{1}{2}\underline{r} | \frac{1}{2}\underline{r}', -\frac{1}{2}\underline{r}')$$

Restriction 5 takes a much simpler form in this case. It is replaced by the two inequalities:

$$\int d^3r d^3r' \omega(\underline{r} - \underline{r}' + \underline{a}, \underline{r} - \underline{r}' - \underline{a}) \geq V^2 |\delta(\underline{a})|^2 - N$$

and:

$$\int d^3r e^{i\mathbf{k} \cdot \underline{r}} \omega(\underline{r} + \underline{a}, \underline{r} - \underline{a}) \geq -\frac{N}{V}$$

which must be valid for all values of the vectors $\underline{a}$ and $\underline{k}$. If N remains fixed as $V \rightarrow \infty$, as is true for nuclear systems, the term $V^2 |\delta(\underline{a})|^2$ may be neglected and thus the whole problem can be expressed in terms of the function ω alone. The diagonal elements of ω give the two-particle correlation function for the system.

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