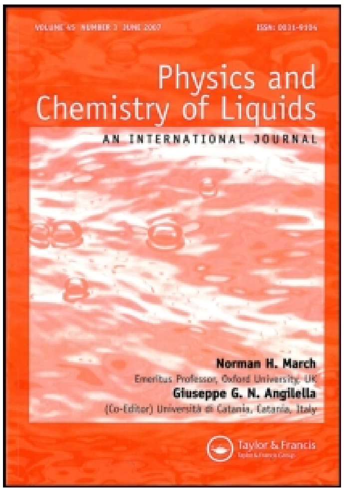

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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A. Holas[a]; N. H. March[b]
[a] Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland [b] Inorganic Chemistry Department, University of Oxford, Oxford, England

To cite this Article Holas, A. and March, N. H.(1996) 'Density Amplitude Equation of Inhomogeneous Electron Liquid: A Route Via Hartree-Fock Density Matrix', Physics and Chemistry of Liquids, 31: 1, 15 — 20
To link to this Article: DOI: 10.1080/00319109608029553
URL: http://dx.doi.org/10.1080/00319109608029553

Phys. Chem. Liq., 1996, Vol. 31, pp. 15–20
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DENSITY AMPLITUDE EQUATION OF INHOMOGENEOUS ELECTRON LIQUID: A ROUTE VIA HARTREE-FOCK DENSITY MATRIX

A. HOLAS[1] and N. H. MARCH[2]

[1]*Institute of Physical Chemistry, Polish Academy of Sciences,*
44/52 Kasprzaka, 01-224 Warsaw, Poland
[2]*Inorganic Chemistry Department, University of Oxford,*
South Parks Road, Oxford OX1 3QR, England

(Received 15 July 1995)

The effective potential entering the Schrödinger equation for the ground-state density amplitude of an inhomogeneous electron liquid is shown to be a unique functional of the Hartree-Fock density matrix, the functional being known. However, this would only become a density functional theory if the Hartree-Fock density matrix could be written as a functional of the exact ground-state density. This is also shown to be true, at least in principle.

KEY WORDS: Electron density amplitude, effective potential, Hartree-Fock density matrix.

1 INTRODUCTION

A long-term aim of modern density functional theory has been to calculate the ground-state electron density $n(\mathbf{r})$ of a many-electron, inhomogeneous assembly without recourse to wave functions. The most promising route to date is to use the density amplitude $n^{1/2}(\mathbf{r})$, which satisfies a Schrödinger equation[1–4]

$$\left\{\frac{-\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r};[n])\right\} n^{1/2}(\mathbf{r}) = \varepsilon n^{1/2}(\mathbf{r}). \tag{1.1}$$

One must, of course, impose normalization in an N-electron system

$$\int d^3r\, n(\mathbf{r}) = N \tag{1.2}$$

and also one will choose that solution of Eq. (1.1) with the lowest eigenenergy. Of course, to exploit this attractive route, one has to know the effective potential v_{eff} as a functional of the density.

This potential is customarily defined as a sum of the Pauli potential v_P and the usual one-body potential of density functional theory[5]–the Slater-Kohn-Sham potential v_{SKS}. Our recent work[6] on the exchange–correlation potential derives v_{xc}, an essential ingredient in v_{SKS}, in terms of low-order density matrices. It remains, of course, a major problem for many-body theory to obtain the density matrices as functionals of $n(\mathbf{r})$. Although some properties of the Pauli potential v_P have already been established[2] and a general procedure for its determination proposed[3] (at the cost of solving $(N-1)$ differential equations) this quantity v_P is still far from being available for practical purposes.

Therefore, in the present paper, we shall demonstrate, by admittedly formal arguments, that $v_{\text{eff}}(\mathbf{r})$ can be characterized solely by the Hartree-Fock (HF) first-order density matrix (written as 1-DM below) shown to be a functional of the density.

2 EQUATION OF MOTION OF HARTREE-FOCK DENSITY MATRIX

In this section we shall therefore define the Hartree-Fock 1-DM via the Hartree–Fock (HF) equations and then determine its equation of motion. The HF equations are conveniently set out in the book by Parr and Yang[5]. They take the form

$$\{\hat{t}_1 + v(\mathbf{r}_1) + v_{\text{es}}(\mathbf{r}_1;[n_{\text{HF}}]) + \hat{v}_X\}\psi_j(\mathbf{x}_1) = \epsilon_j\psi_j(\mathbf{x}_1), \quad j = 1,2\ldots N. \tag{2.1}$$

Here $\mathbf{x}_1$ denotes space plus spin coordinates $(\mathbf{r}_1, s_1)$, $\hat{t}_1 = -(\hbar^2/2m)\nabla_1^2$, $v(\mathbf{r})$ is the external potential, while v_{es} is the classical electrostatic potential

$$v_{\text{es}}(\mathbf{r}_1;[n_{\text{HF}}]) = \int d^3r_2\, u(\mathbf{r}_1 - \mathbf{r}_2) n_{\text{HF}}(\mathbf{r}_2);\ u(\mathbf{r}) = e^2/|\mathbf{r}|. \tag{2.2}$$

The unique feature of the HF equations is the presence of $\hat{v}_X$, the HF exchange integral operator (a non-local potential)

$$(\hat{v}_X\psi)(\mathbf{x}_1) = -\int d\mathbf{x}_2\, u(\mathbf{r}_1 - \mathbf{r}_2)\gamma_{\text{HF}}(\mathbf{x}_1;\mathbf{x}_2)\psi(\mathbf{x}_2) \tag{2.3}$$

where the notation $\int d\mathbf{x}_j \cdots = \sum_{s_j} \int d^3r_j \cdots$ is employed.

Then the key tool of this paper, the HF 1-DM corresponding to the solutions of Eq. (2.1) is

$$\gamma_{\text{HF}}(\mathbf{x}_1;\mathbf{x}_1') = \sum_{j=1}^{N} \psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1') \tag{2.4}$$

and this leads to the HF density on the diagonal as

$$n_{\text{HF}}(\mathbf{r}) = \sum_s \gamma_{\text{HF}}(\mathbf{r}s;\mathbf{r}s). \tag{2.5}$$

The N equations (2.1) must be solved self-consistently, since both v_{es} and $\hat{v}_X$ depend on N normalized solutions $\psi_j(x)$.

We now proceed to construct the equation of motion of the HF 1-DM. As a first step, let us multiply Eq. (2.1) by $\psi_j^*(\mathbf{x}_1')$ and use Eq. (2.2) – (2.5). Then one can show that

$$\{\hat{t}_1 + v(\mathbf{r}_1) - \epsilon_j\}\, \psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1')$$
$$+ \int d\mathbf{x}_2 u(\mathbf{r}_1 - \mathbf{r}_2)[\gamma_{\mathrm{HF}}(\mathbf{x}_2;\mathbf{x}_2)\psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1') - \gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_2)\psi_j(\mathbf{x}_2)\psi_j^*(\mathbf{x}_1')] = 0. \quad (2.6)$$

The next step involves taking the complex conjugate of this equation and then relabelling the variables according to $\mathbf{x}_1 \rightleftarrows \mathbf{x}_1'$ to obtain

$$\{\hat{t}_{1'} + v(\mathbf{r}_1) \ - \epsilon_j\}\, \psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1')$$
$$+ \int d\mathbf{x}_2 u(\mathbf{r}_1' - \mathbf{r}_2)[\gamma_{\mathrm{HF}}(\mathbf{x}_2;\mathbf{x}_2)\psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1') - \gamma_{\mathrm{HF}}(\mathbf{x}_2;\mathbf{x}_1')\psi_j(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)] = 0. \quad (2.7)$$

The final step to the equation of motion for γ_{HF} is to subtract Eq. (2.7) from (2.6) and then to sum over j up to N. This then yields the desired result in the form

$$\{[\hat{t}_1 + v(\mathbf{r}_1)] - [\hat{t}_{1'} + v(\mathbf{r}_1')]\}\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1')$$
$$+ 2\int d\mathbf{x}_2 \{u(\mathbf{r}_1 - \mathbf{r}_2) - u(\mathbf{r}_1' - \mathbf{r}_2)\}\gamma_{\mathrm{HF}}^{(2)}(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_1'\mathbf{x}_2) = 0. \quad (2.8)$$

Here $\gamma_{\mathrm{HF}}^{(2)}$, the combination of the HF 1-DM known as the HF second-order density matrix (2-DM), has been introduced as in ref. 5:

$$\gamma_{\mathrm{HF}}^{(2)}(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_1'\mathbf{x}_2') = \frac{1}{2}\{\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1')\gamma_{\mathrm{HF}}(\mathbf{x}_2;\mathbf{x}_2') - \gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_2')\gamma_{\mathrm{HF}}(\mathbf{x}_2;\mathbf{x}_1')\}. \quad (2.9)$$

It is of interest to stress that the equation of motion (2.8) for γ_{HF} is of exactly the form of the equation for the exact interacting 1-DM obtained earlier by Dawson and March[7]. Of course, the exact $\gamma^{(2)}$ in their equation replaces the HF 2-DM present in Eq. (2.8).

2. 1 *Relation between external potential and HF 1-density matrix*

What we note in the present context in that Eq. (2.8), when used in conjuction with (2.9), gives a relation between the external potential and the HF 1-DM:

$$v(\mathbf{r}_1) = v(\mathbf{r}_1') - \frac{(\hat{t}_1 - \hat{t}_{1'})\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1') + 2\int d\mathbf{x}_2[u(\mathbf{r}_1 - \mathbf{r}_2) - u(\mathbf{r}_1' - \mathbf{r}_2)]\gamma_{\mathrm{HF}}^{(2)}(\mathbf{x}_1\mathbf{x}_2;\mathbf{x}_1'\mathbf{x}_2)}{\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1')} \quad (2.10)$$

The form of Eq.(2.10) demonstrates that the potential is fixed to within an additive constant only. We can arbitrarily choose a reference point $\mathbf{r}_1'$ (e.g. at infinity), the value of the potential there (e.g. zero) and also a pair of spin indices s_1, s_1'. Then Eq.(2.10) allows the reconstruction of the external potential v from knowledge of the

Hartree-Fock idempotent density matrix (1-DM):

$$v = \hat{v}\,[\gamma_{\mathrm{HF}}]. \tag{2.11}$$

This is the first important conclusion of the present work.

3 CONSTRUCTION OF EFFECTIVE POTENTIAL IN EQN. (1.1)

In order to use this information to construct v_{eff} in Eq. (1.1), let us recall the formal derivation of this equation. The Euler-Lagrange equation

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu, \tag{3.1}$$

where μ is the constant chemical potential, at every point in the inhomogeneous charge cloud of the electron liquid, follows from the variational principle of the Hohenberg-Kohn[8] formulation of the ground-state problem. Their work proves the existence of the universal functional $F[n]$, although its explicit form remains unknown. Eq. (3.1) tells us, on the one hand, that the external potential can be reconstructed, in principle, to within an additive constant, from a given ground-state density:

$$v(\mathbf{r}) = \mu - \frac{\delta F[n]}{\delta n(\mathbf{r})}. \tag{3.2}$$

On the other hand, provided $F[n]$ becomes known eventually with sufficient accuracy, the ground-state density n of the inhomogeneous electronic assembly, characterized by external potential v, could be obtained by solution of Eq. (3.1).

Let us next transform Eq. (3.1) somewhat by adding and subtracting the functional derivative of the von Weizsäcker kinetic energy $T_{\mathrm{W}}[n]$. This is defined as

$$T_{\mathrm{W}}[n] = \int d^3r\, t_{\mathrm{W}}(\mathbf{r};[n]) \tag{3.3}$$

where

$$t_{\mathrm{W}}(\mathbf{r};[n]) = \frac{\hbar^2}{2m}|\nabla n^{1/2}(\mathbf{r})|^2 = \frac{\hbar^2}{8m}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}. \tag{3.4}$$

The functional derivative can readily be calculated as

$$\frac{\delta T_{\mathrm{W}}[n]}{\delta n(\mathbf{r})} = -\frac{\hbar^2}{2m}\frac{\nabla^2 n^{1/2}(\mathbf{r})}{n^{1/2}(\mathbf{r})} = \frac{\hbar^2}{8m}\left(\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}\right)^2 - \frac{\hbar^2}{4m}\frac{\nabla^2 n(\mathbf{r})}{n(\mathbf{r})}. \tag{3.5}$$

Hence Eq. (3.1) can be rewritten as

$$-\frac{\hbar^2}{2m}\frac{\nabla^2 n^{1/2}(\mathbf{r})}{n^{1/2}(\mathbf{r})} + v_{\mathrm{eff}}(\mathbf{r};[n]) = \mu, \tag{3.6}$$

which is identical with the Schrödinger Eq. (1.1) for the electron density amplitude.

The effective potential then takes the form

$$v_{\mathrm{eff}}(\mathbf{r};[n])=\frac{\delta F[n]}{\delta n(\mathbf{r})}-\frac{\delta T_{\mathrm{W}}[n]}{\delta n(\mathbf{r})}. \tag{3.7}$$

The following chain of relations then allow the connection of the effective potential v_{eff} with the Hartree-Fock density matrix:

(i) From Eq. (3.2) it follows that $v(\mathbf{r})$ is a functional of $n(\mathbf{r})$.
(ii) By solution of the HF Eqs. (2.1), the eigenfunctions and in particular their combination $\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1')$ in Eq. (2.4) are demonstrated to be functionals of the external potential $v(\mathbf{r})$.
(iii) Therefore the HF 1-DM is a functional of the ground-state density of the same system

$$\gamma_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1')=\tilde{\gamma}_{\mathrm{HF}}(\mathbf{x}_1;\mathbf{x}_1';[n]). \tag{3.8}$$

(iv) The interpretation (2.11) of Eq. (2.10), combined with Eq. (3.8) establishes that

$$v=\tilde{v}[\tilde{\gamma}_{\mathrm{HF}}[n]]. \tag{3.9}$$

(v) Because of the relation (3.2), we can substitute the negative of $\tilde{v}[\tilde{\gamma}_{\mathrm{HF}}[n]]$ into Eq. (3.7) in order to obtain finally the effective potential in terms of the Hartree–Fock density matrix as

$$v_{\mathrm{eff}}(\mathbf{r};[n])=-\tilde{v}(\mathbf{r};[\tilde{\gamma}_{\mathrm{HF}}[n]])-\frac{\delta T_{\mathrm{W}}[n]}{\delta n(\mathbf{r})}. \tag{3.10}$$

The right-hand side of Eq. (3.10) is given by the explicit expression (2.10) for the first term and by Eq. (3.5) for the second contribution: however the explicit form of the relation (3.8) remains unknown.

4 SUMMARY

The main results of this paper are summarized in Eqs. (2.10) and in (3.10). It must be emphasized that the proof of the last result remains at the level of formal existence theorem. Of course, to use the results on practical examples of an inhomogeneous electron liquid, some approximation to the relation (3.8) must be constructed. But at least one knows the HF 1-DM to a prescribed numerical accuracy, in medium sized atoms and molecules, to use as a starting point.

Acknowledgements

This work was brought to fruition while both authors were present at ICTP Trieste in the Research Workshop on Condensed Matter, 1995. They wish to thank Professor Yu Lu and his colleagues for hospitality and for much stimulating discussion.

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