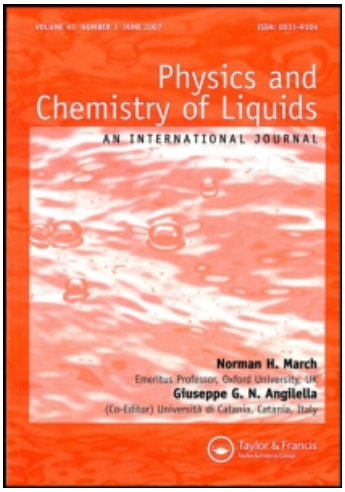

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Amovilli, C. , March, N. H. , Schmalz, T. G. , Hite, G. and Klein, D. J.(1999) 'Inhomogeneous Electron Liquid: Differential Equation Satisfied by Diagonal Element of Coulomb Bound *s*-State Green Function', Physics and Chemistry of Liquids, 37: 4, 475 — 478
To link to this Article: DOI: 10.1080/00319109908031452
URL: http://dx.doi.org/10.1080/00319109908031452

Phys. Chem. Liq., 1999, Vol. 37, pp. 475 - 478
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Letter

INHOMOGENEOUS ELECTRON LIQUID: DIFFERENTIAL EQUATION SATISFIED BY DIAGONAL ELEMENT OF COULOMB BOUND *s*-STATE GREEN FUNCTION

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(Received 1 March 1998)

Because of density functional theory, attention has shifted from density matrices and Green functions to their diagonal elements. Here, an explicit partial differential equation is given for the diagonal elements of the bound state Green function for the *s*-states only. Relation to earlier work in terms of Whittaker functions is briefly discussed, for the Coulomb field case.

Keywords: Electron liquid; bound *s*-state Green function

Early work by March and Murray [1] was concerned with the canonical density matrix $C(\vec{r},\vec{r}';\beta)(\beta = 1/k_B T)$, and its diagonal element, the so-called Slater sum $S(\vec{r},\beta)$, in central field problems. While $C(\vec{r},\vec{r}';\beta)$ satisfies the Bloch equation, in Ref. [1] it was shown that the analysis of $S(\vec{r},\beta)$ into partial waves allowed an explicit partial differential equation to be constructed for $S_l(r,\beta)$, with l the orbital angular momentum quantum number. In the present study, the

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result for $l = 0$ in Ref. [1] is utilized to study the Coulomb Green function. The usual definition of this quantity involves a sum over the entire level spectrum, which for this hydrogen-like system is an inifite number of bound states plus continuum. Precisely, the bound-state Coulomb Green function for s-states only is defined by

$$G_{\mathrm{bs}}(\vec{r}, \vec{r}'; E) = \sum_{n=1}^{\infty} \frac{\psi_{n00}(\vec{r})\psi^*_{n00}(\vec{r}')}{E + (Z^2/2n^2) + i\eta} \quad (\eta \to 0); \tag{1}$$

i.e., with the sum of the hydrogenic wave function product for $l = m = 0$ over the energy denominator restricted to bound-states only.

Our primary aim below is to set up a differential equation for the diagonal element $G_{\mathrm{bs}}(r, E) \equiv G_{\mathrm{bs}}(\vec{r}, \vec{r}; E)$ of this quantity (1). To do so, it will be convenient to construct $G_{\mathrm{bs}}(r, E)$ from the bound-state Slater sum. This is defined, again for s-states only, as

$$S_{\mathrm{bs}}(r, \beta) = \sum_{n=1}^{\infty} \psi_{n00}(r)\psi^*_{n00}(r) \exp\left(\frac{\beta Z^2}{2n^2}\right). \tag{2}$$

In Ref. [1] an explicit partial differential equation was constructed for $S_{\mathrm{bs}}(r, \beta)$, namely

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2 S_{\mathrm{bs}}) - \frac{1}{2}\frac{\partial V}{\partial r}(r^2 S_{\mathrm{bs}}) - V\frac{\partial}{\partial r}(r^2 S_{\mathrm{bs}}) - \frac{\partial^2}{\partial\beta\partial r}(r^2 S_{\mathrm{bs}}) = 0 \tag{3}$$

which has been rederived in the later work of Cooper [2]. Equation (3) is true for a general central potential $V(r)$: here we specialize to $V = -Z/r$. In this special case the s-states determine the entire Slater sum.

Let us now take the Laplace transform of Eq. (2) with respect to β:

$$\begin{aligned} \mathcal{L}S_{\mathrm{bs}}(r, \beta) &= \sum_{n=1}^{\infty} \psi_{n00}(r)\psi^*_{n00}(r) \int_0^{\infty} \exp\left(\frac{\beta Z^2}{2n^2}\right) \exp(-\beta E) d\beta \\ &= \sum_{n=1}^{\infty} \frac{\psi_{n00}(r)\psi^*_{n00}(r)}{-E + (Z^2/2n^2)}. \end{aligned} \tag{4}$$

Comparison of Eq. (4) with the diagonal element $\vec{r}' = \vec{r}$ of Eq. (1) shows that

$$\mathcal{L}S_{\mathrm{bs}}(r, \beta) = G_{\mathrm{bs}}(r, -E) \tag{5}$$

for the bare Coulomb field case.

Thus, the primary objective of the work, namely to establish a differential equation for the bound-state Green function, is equivalent to deriving the differential equation satisfied by $\mathcal{L}S_{\rm bs}(r,\beta)$. But this can now be achieved by taking the Laplace transform $\mathcal{L}$ of Eq. (3) with respect to β

This yields, with $\mathcal{L}_s \equiv \mathcal{L}S_{\rm bs}(r,\beta)$

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2\mathcal{L}_s) - \frac{1}{2}\frac{\partial V}{\partial r}(r^2\mathcal{L}_s) - V\frac{\partial}{\partial r}(r^2\mathcal{L}_s) - \frac{\partial}{\partial r}r^2\int_0^\infty \left(\frac{\partial S_{\rm bs}}{\partial \beta}\right)\exp(-\beta E)d\beta = 0. \tag{6}$$

Integrating by parts in Eq. (6) gives for the final term on the LHS the value

$$-\frac{\partial}{\partial r}r^2\left\{[S_{\rm bs}(r,\beta)\exp(-\beta E)]_0^\infty + E\int_0^\infty S_{\rm bs}(r,\beta)\exp(-\beta E)d\beta\right\} = = -\frac{\partial}{\partial r}r^2[-S_{\rm bs}(r,0) + E\mathcal{L}_s]. \tag{7}$$

But one can now remove the term in $S_{\rm bs}(r,0)$ by inserting Eq. (7) into Eq. (6) and then by differentiation with respect to E.

Denoting $\partial\mathcal{L}/\partial E$ by $\mathcal{L}'$ one finds

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2\mathcal{L}'_s) - \frac{1}{2}\frac{\partial V}{\partial r}(r^2\mathcal{L}'_s) - V\frac{\partial}{\partial r}(r^2\mathcal{L}'_s) - \frac{\partial}{\partial r}(r^2\mathcal{L}_s) - E\frac{\partial}{\partial r}(r^2\mathcal{L}'_s) = 0. \tag{8}$$

This from Eq. (5), essentially provides the desired partial differential equation for $G_{\rm bs}(r,-E)$, and Eq. (8) is the central result of this Letter.

It is relevant in the present context to note that, for the Coulomb potential $-Z/r$ considered here, Ho and Inomata [3] have given a closed form of the usual s-state Green function $G_s(\vec{r},\vec{r}';E)$ in which both bound and continuum states are included in the summation of the terms in Eq. (1). On the diagonal $\vec{r}=\vec{r}'$, their result has the following shape:

$$r^2G_s(r,E) = f(E)MW \tag{9}$$

where M and W are solutions of Whittaker's equation

$$\frac{d^2\omega}{dz^2} + \left(-\frac{1}{4} + \frac{\kappa}{z} + \frac{(1/4) - \mu^2}{z^2} \right) \omega = 0 \tag{10}$$

for appropriate choices of κ and μ, and $f(E)$ is known. If one could project out of their closed result (9) the bound states, then one would naturally have an explicit solution of Eq. (8), but we shall not pursue the matter further in this Letter.

In summary, density functional theory of an inhomogeneous electron liquid focusses directly on the diagonal density $\rho(\vec{r})$ instead of the off-diagonal pure state density matrix $\gamma(\vec{r}, \vec{r}')$ (see Theophilou and March [4] for the Coulomb field case). Here, this philosophy, applied in Ref. [1] already to the canonical density matrix C and the s-state Slater sum, has been extended to the off-diagonal s-state Green function $G_{\mathrm{bs}}(\vec{r}, \vec{r}'; E)$ for bound states only in Eq. (1). A differential equation has here been constructed for its diagonal part $G_{\mathrm{bs}}(r, -E)$. This Eq. (8) may be related to a form such as given in Eq. (9), but as it stands this result of Ho and Inomata [3] includes continuum as well as the bound states solely considered in this Letter.

Acknowledgement

One of us (NHM) wishes to acknowledge that his contribution to the present study was brought to fruition during a visit to Texas A&M University at Galveston. DJK and TGS acknowledge support from the Welch Foundation.

References

[1] March, N. H. and Murray, A. M. (1960). *Phys Rev.*, **120**, 830.
[2] Cooper, I. L. (1994). *Phys. Rev.*, **A50**, 1040.
[3] Ho, R. and Inomata, A. (1982). *Phys. Rev. Lett.*, **48**, 231.
[4] Theophilou, A. K. and March, N. H. (1986). *Phys. Rev.*, **A34**, 3630.