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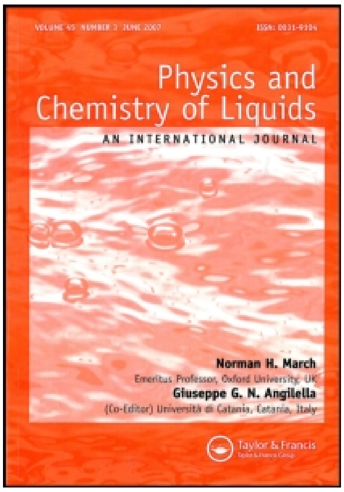

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Letter

Pauli and Exchange Potentials for Determining Density Amplitude in an Inhomogeneous Electron Liquid

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To calculate the electron density amplitude $\rho^{1/2}$ in an inhomogeneous electron liquid, use of the local potential $V(\mathbf{r})$ of density functional theory is equivalent to solving a Schrödinger equation for $\rho^{1/2}$ with potential $V(\mathbf{r}) + V_{\text{Pauli}}(\mathbf{r})$. A first-principles justification is given for the parameterized form

$$V_{\text{Pauli}}(\mathbf{r}) = \frac{\hbar^2}{m}[\alpha_1\rho^{2/3} + \beta_1\{(\nabla\rho)^2/\rho^2\} + \beta_2(\nabla^2\rho/\rho)].$$

Key Words: Electron density amplitude, Pauli potential, exchange potential, electron liquid.

Some attention has been given in this Journal recently to properties of an electron liquid, and in particular to (a) the pair function and structure factor of an interacting electron liquid[1] and (b) the electron density of an atom embedded in an originally uniform electron liquid.[2] The present letter is in the same general area, dealing as it does with electron density in an inhomogeneous electron assembly. We first note that some time ago, the writer and Murray[3] utilized the fact that in the simplest density functional theory of Thomas and Fermi,[4] with the kinetic energy corrected by the inhomogeneity term $\hbar^2/8m \int (\nabla\rho)^2/\rho \, d\mathbf{r}$ of von Weizsäcker, the density amplitude $\rho^{1/2} \equiv \psi$ of the ground-state density $\rho(\mathbf{r})$ satisfies a Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(\varepsilon - \mathcal{V}(\mathbf{r}))\psi = 0 \qquad (1)$$

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where the effective potential $\mathscr{V}(\mathbf{r})$ in the treatment was the original potential $V(\mathbf{r})$, plus a contribution $V_p(\mathbf{r})$, subsequently termed the Pauli potential[5]

$$\mathscr{V}(\mathbf{r}) = V(\mathbf{r}) + V_p(\mathbf{r}). \tag{2}$$

In the Thomas–Fermi–von Weizsäcker approximation, it was demonstrated in Ref. 3 that

$$V_p^{\mathrm{TFW}}(\mathbf{r}) = \tfrac{5}{3}c_k\rho^{2/3}(\mathbf{r}) \tag{3}$$

with c_k as in Eq. (7) below.

Subsequently, the writer has shown that the Pauli potential can be written, to within an additive constant, in the formally exact manner:[5]

$$V_p(\mathbf{r}) = \frac{\delta T_s}{\delta\rho(\mathbf{r})} + \frac{\hbar^2}{4m}\frac{\nabla^2\rho}{\rho} - \frac{\hbar^2}{8m}\frac{(\nabla\rho)^2}{\rho^2}, \tag{4}$$

$T_s[\rho]$ being the single-particle kinetic energy as a functional of ρ. Other workers have also contemplated determining the exact density $\rho(\mathbf{r})$ from a Schrödinger equation; especially notable contributions being those of Hunter[6] and of Levy *et al.*[7]

Since T_s is not known exactly, it is often bypassed, as in Slater's work,[8] which was formally completed by Kohn and Sham,[9] by returning to a set of single-particle equations for one-electron functions and solving them with the one-body potential $V(\mathbf{r})$. In the present work, what is proposed is to insert into Eq. (4) a specific approximation to $\delta T_s/\delta\rho(\mathbf{r})$ recently set up by the author.[10] In this work, the exchange potential $V_x(\mathbf{r})$ is written in terms of the kinetic energy density t and $\delta T_s/\delta\rho(\mathbf{r})$, where $T_s = \int t\,d\mathbf{r}$, by using again slowly varying electron density theory, resembling the Thomas–Fermi–Dirac method.[4] Then one finds the approximate relation

$$\frac{\delta T_s}{\delta\rho(\mathbf{r})} = \frac{t^2V_x}{D\rho^3} - \frac{Ct}{D\rho}. \tag{5}$$

By requiring that Eq. (5) becomes exact in the sense of reproducing precisely the Hartree–Fock ground-state energy of the uniform gas, it is readily shown that the constants C and D are related by

$$C + \tfrac{5}{3}D = -\tfrac{4}{3}c_kc_e. \tag{6}$$

In Eq. (6), c_k and c_e are respectively the kinetic and exchange constants characterizing the uniform electron gas: namely[4]

$$c_k = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} : c_e = \tfrac{3}{4}e^2\left(\frac{3}{\pi}\right)^{1/3}. \tag{7}$$

Inserting Eq. (5) into the formally exact Eq. (4), the Pauli potential is related to the exchange potential V_x by

$$V_p(\mathbf{r}) = \frac{V_x t^2}{D\rho^3} - \frac{Ct}{D\rho} + \frac{\hbar^2}{4m}\frac{\nabla^2\rho}{\rho} - \frac{\hbar^2}{8m}\frac{(\nabla\rho)^2}{\rho^2}. \tag{8}$$

Since t is not known exactly, as already mentioned above, let us employ in this approximate Eq. (8) the low-order gradient expansion[5]

$$t = c_k\rho^{5/3} + \frac{\lambda\hbar^2}{8m}\frac{(\nabla\rho)^2}{\rho} + \cdots \tag{9}$$

where $\lambda = 1$ according to von Weizsäcker[4] but was later calculated by Kirznits[11] as $\frac{1}{9}$ for a slowly varying electron density distribution. Then, using for V_x the well-established Dirac–Slater form, though non-local theories do exist,[12]

$$V_x = -\gamma\rho^{1/3} \tag{10}$$

where γ is allowed, following Slater[13] to vary from the Dirac value $\frac{4}{3}c_e$, one is led almost immediately to the form

$$V_p(\mathbf{r}) = \frac{\hbar^2}{m}\left[\alpha_1\rho^{2/3}(\mathbf{r}) + \beta_1\frac{(\nabla\rho)^2}{\rho^2} + \beta_2\frac{\nabla^2\rho}{\rho}\right]. \tag{11}$$

Equation (8), and its more tractable approximate form (11), constitute the main results of the present work. Evidently, Eq. (11) contains the result (3) given by March and Murray[3] if the parameters are chosen such that $(\hbar^2/m)\alpha_1 = \frac{5}{3}c_k$ and $\beta_1 = \beta_2 = 0$. The Kirznits form of the Pauli potential, derived in Ref. 5, corresponds to the same choice of α_1 but to $\beta_1 = -\frac{1}{2}\beta_2$; $\beta_2 = (1 - \lambda)$, with $\lambda = \frac{1}{9}$. The present approach shows, however, that first principles justification can be given for varying α_1 from the von Weizsäcker–Kirznits value.

It would seem, therefore, to be of considerable interest to study, say, the series of closed shell atoms Ne–Xe, as well as atoms embedded in jellium,[2] in which the density $\rho(\mathbf{r})$ and the one-body potential $V(\mathbf{r})$ are calculated from standard density functional theory based on one-electron wave functions. With neglect of correlation, one would have

$$V(\mathbf{r}) = V_{\text{Hartree}}(\mathbf{r}) + V_x(\mathbf{r}) \tag{12}$$

with V_x taken to be proportional to $\rho^{1/3}(\mathbf{r})$, with appropriate choice of the Slater parameter α.[13] The question then arises whether, by choice of a single set of parameters α_1, β_1 and β_2 in Eq. (11), all the significant features, and especially the shell structure, of the electron density profiles can be reproduced by direct solution of the Schrödinger Eq. (1).

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Of course, in the variation of parameters, the specific values $(\hbar^2/m)\alpha_1 = \frac{5}{3}c_k$ in Eq. (3) and $\beta_2 = \frac{1}{4}$ in Eq. (8), offer useful guidelines, but one would wish especially to exploit the flexibility of varying β_1 in conjunction with small deviations of α_1 from the von Weizsäcker–Kirznits value.

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