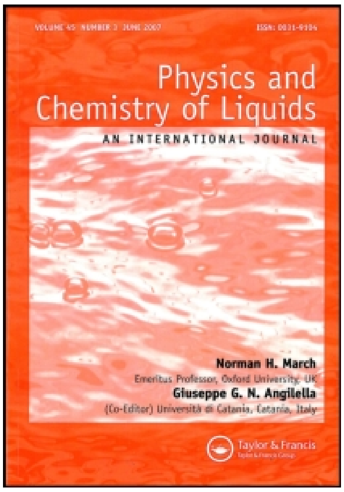

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Proposed approximate relation in inhomogeneous electron liquids between exchange-only potential and its Slater counterpart

N. H. March[a][b]; Á. Nagy[c]
[a] Department of Physics, University of Antwerp, Antwerp, Belgium [b] Oxford University, Oxford, UK [c] Department of Theoretical Physics, University of Debrecen, H-4010 Debrecen, Hungary

To cite this Article March, N. H. and Nagy, Á.(2010) 'Proposed approximate relation in inhomogeneous electron liquids between exchange-only potential and its Slater counterpart', Physics and Chemistry of Liquids, 48: 5, 648 — 651

To link to this Article: DOI: 10.1080/00319101003646587

URL: http://dx.doi.org/10.1080/00319101003646587

Physics and Chemistry of Liquids
Vol. 48, No. 5, October 2010, 648–651

Proposed approximate relation in inhomogeneous electron liquids between exchange-only potential and its Slater counterpart

N.H. March[a][b] and Á. Nagy[c]*

[a]*Department of Physics, University of Antwerp, Antwerp, Belgium;* [b]*Oxford University, Oxford, UK;* [c]*Department of Theoretical Physics, University of Debrecen, H–4010 Debrecen, Hungary*

(*Received 22 January 2010; final version received 23 January 2010*)

We consider here exchange-only density functional theory. The search for the exchange-only potential $V_x(\mathbf{r})$ involves either the optimal effective potential, or as an approximate alternative, calculating corrections to the Slater (Sl) potential $V_x^{\mathrm{Sl}}(\mathbf{r}) = 2e_x(\mathbf{r})/n(\mathbf{r})$, $e_x(\mathbf{r})$ and $n(\mathbf{r})$ being, respectively, the exchange energy density due to Dirac and the ground-state electron density. The Levy–Perdew virial-like integral relation between the total exchange energy and the gradient of $V_x(\mathbf{r})$ is an important element in the present proposal.

Keywords: exchange-only potential; Slater form; correlation corrections

1. Introduction

Recently, we have proposed an approximate differential form of a version of the Levy–Perdew (LP) relation [1] between the total exchange energy, E_x, and the exchange potential, $V_x(\mathbf{r})$. This LP relation reads

$$E_x = -\int n(\mathbf{r})\mathbf{r}\cdot\frac{\partial V_x(\mathbf{r})}{\partial \mathbf{r}}\mathrm{d}\mathbf{r}. \tag{1}$$

This was in our earlier work integrated by parts to yield [2]

$$E_x = \int\left[3n(\mathbf{r}) + \mathbf{r}\cdot\frac{\partial n(\mathbf{r})}{\partial \mathbf{r}}\right]V_x(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{2}$$

The differential form we proposed, denoted by $e_X^{MN}(\mathbf{r})$, will be written in the form

$$e_x^{MN}(\mathbf{r}) = \left[3n(\mathbf{r}) + \mathbf{r}\cdot\frac{\partial n(\mathbf{r})}{\partial \mathbf{r}}\right]V_x(\mathbf{r}) = \frac{1}{2}V_x^{\mathrm{Sl}}(\mathbf{r})n(\mathbf{r}) + S(\mathbf{r}), \tag{3}$$

where the Slater (Sl) exchange potential [3] designed to approximate $V_x(\mathbf{r})$ takes the form

$$V_x^{\mathrm{Sl}}(\mathbf{r}) = \frac{2e_x(\mathbf{r})}{n(\mathbf{r})}, \tag{4}$$

---

*Corresponding author. Email: anagy@madget.atomki.hu

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319101003646587
http://www.informaworld.com

while $S(\mathbf{r})$ satisfies the integral condition $\int S(\mathbf{r})\mathrm{d}\mathbf{r} = 0$. Here $e_x(\mathbf{r})$ is taken to be defined by the Dirac formula [4]

$$e_x(\mathbf{r}) = -\frac{e^2}{4}\int \frac{\gamma_s(\mathbf{r},\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}', \tag{5}$$

$\gamma_s(\mathbf{r},\mathbf{r}')$ being the single-particle (s) idempotent Dirac density matrix.

2. Use of formally exact integral equation theory for exchange-only potential $V_x(\mathbf{r})$

We next appeal to the integral equation theory of $V_x(\mathbf{r})$ proposed by Della-Sala and Görling [5] (see also [6]) and formally completed by Howard and March [7] (see also [8]). This reads

$$\begin{aligned} V_x(\mathbf{r}) = V_x^{\mathrm{Sl}}(\mathbf{r}) &+ \frac{1}{2n(\mathbf{r})}\int \mathrm{d}\mathbf{r}'|\gamma_s(\mathbf{r},\mathbf{r}')|^2 V_x(\mathbf{r}') \\ &+ \frac{e^2}{4n(\mathbf{r})}\int\int \mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}'' \frac{\gamma_s(\mathbf{r},\mathbf{r}')\gamma_s(\mathbf{r},\mathbf{r}'')\gamma_s(\mathbf{r}''\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}''|} + \frac{P(\mathbf{r})}{n(\mathbf{r})}, \end{aligned} \tag{6}$$

where $P(\mathbf{r})$ satisfies the integral condition [7]

$$\int P(\mathbf{r})\mathrm{d}\mathbf{r} = 0. \tag{7}$$

At this point, let us return to Equation (3) to find

$$6A(\mathbf{r})V_x(\mathbf{r}) = V_x^{\mathrm{Sl}}(\mathbf{r}) + \frac{2S(\mathbf{r})}{n(\mathbf{r})}, \tag{8}$$

$A(\mathbf{r})$ being defined as

$$A(\mathbf{r}) = 1 + \frac{\mathbf{r}\cdot\nabla n(\mathbf{r})}{3n(\mathbf{r})}. \tag{9}$$

Now our aim is to bypass the integral equation form in Equation (6) by substituting $V_x(\mathbf{r})$ appearing in the RHS of Equation (6) using Equation (8). This then yields

$$\begin{aligned} V_x(\mathbf{r}) = V_x^{\mathrm{Sl}}(\mathbf{r}) &+ \frac{1}{12n(\mathbf{r})}\int \mathrm{d}\mathbf{r}'|\gamma_s(\mathbf{r},\mathbf{r}')|^2 A(\mathbf{r}')^{-1}\left[V_x^{\mathrm{Sl}}(\mathbf{r}') + \frac{2S(\mathbf{r}')}{n(\mathbf{r}')}\right] \\ &+ \frac{e^2}{4n(\mathbf{r})}\int\int \mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}'' \frac{\gamma_s(\mathbf{r},\mathbf{r}')\gamma_s(\mathbf{r},\mathbf{r}'')\gamma_s(\mathbf{r}'',\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}''|} + \frac{P(\mathbf{r})}{n(\mathbf{r})}. \end{aligned} \tag{10}$$

Of course, the price paid in writing the form (10) is that not only does the function $P(\mathbf{r})$ entering Equations (6) and (7) appear, but also $S(\mathbf{r})$ introduced in Equation (3).

The 'zeroth order' approximation for $P(\mathbf{r})$ is the proposal of Della-Sala and Görling [5] that it be put to zero. As these authors stress, it is equivalent to what seems to us the drastic approximation that the Slater–Kohn–Sham determinant equals its Hartree–Fock counterpart. However, it is relevant here to note that the 'denominator' approximation of Gritsenko and Baerends [6] yields the same result as the later work of Della-Sala and Görling [5]. It is also tempting to try the choice $S(\mathbf{r}) = 0$ in addition, but below we shall attempt to transcend this by appealing to the work of Solomatin *et al.* [9]. These workers studied the exchange-only potential V_x in a simple model of a metal surface, and we give a concise summary of their results immediately below. These authors divide $V_x(\mathbf{r})$ into the sum of two parts which they write as

$$V_x(\mathbf{r}) = V_x^0(\mathbf{r}) + f(\mathbf{r}). \tag{11}$$

$f(\mathbf{r})$ is known to satisfy the exact sum rule (equation (2) of [9])

$$\int \mathrm{d}\mathbf{r} n(\mathbf{r})\mathbf{r} \cdot \nabla f(\mathbf{r}) = 0. \tag{12}$$

They use $A(\mathbf{r})$ defined in Equation (9) to express the part $V_x^0(\mathbf{r})$ in Equation (11) as

$$6n(\mathbf{r})A(\mathbf{r})V_x^0(\mathbf{r}) = 4n(\mathbf{r})V_x^{\mathrm{Sl}}(\mathbf{r}) + \mathbf{r} \cdot \nabla[n(\mathbf{r})V_x^{\mathrm{Sl}}(\mathbf{r})]. \tag{13}$$

In their original study, Solomatin *et al.* [9] expect Equation (13) to be already an accurate representation of $V_x(\mathbf{r})$ at a metal surface, for precise reasons involving asymptotic behaviour set out in their article. Returning to the present proposal in (8), this would then be equivalent to the approximation for $S(\mathbf{r})$ given from Equation (13) by

$$S(\mathbf{r}) = -\frac{1}{2}n(\mathbf{r})V_x^{\mathrm{Sl}}(\mathbf{r}) + 3A(\mathbf{r})n(\mathbf{r})(V_x^0(\mathbf{r}) + f(\mathbf{r})), \tag{14}$$

where $V_x^0(\mathbf{r})$ is given explicitly by Equation (13). We can readily evaluate the volume integral of $S(r)$ from Equation (14). Obviously, as already known to Slater [3], the first term on the RHS of Equation (14) yields minus the total exchange energy. Applying the sum rule (12) for $f(\mathbf{r})$, we arrive at the expected result: $\int S(\mathbf{r})\mathrm{d}\mathbf{r} = 0$.

3. Approximate inclusion of electron correlation

To conclude, we want to refer to the generalisation of the result (1) above to include electron correlation. This reads [1]

$$E_{xc} + T_c = -\int n(\mathbf{r})\mathbf{r} \cdot \frac{\partial V_{xc}(\mathbf{r})}{\partial \mathbf{r}}\mathrm{d}\mathbf{r}, \tag{15}$$

which we write in the differential form

$$e_{xc}(\mathbf{r}) + t_c(\mathbf{r}) = \left[3n(\mathbf{r}) + \mathbf{r} \cdot \frac{\partial n(\mathbf{r})}{\partial \mathbf{r}}\right]V_{xc}(\mathbf{r}) + C(\mathbf{r}), \tag{16}$$

where

$$E_{xc} = \int e_{xc}(\mathbf{r})\mathrm{d}\mathbf{r}, \qquad T_c = \int t_c(\mathbf{r})\mathrm{d}\mathbf{r}, \qquad \int C(\mathbf{r})\mathrm{d}\mathbf{r} = 0. \tag{17}$$

Evidently, *xc* now denotes the exchange plus correlation, while T_c is the total kinetic correlation energy.

As an example let us choose the He atom, discussed in [10]. These workers gave what they believe to be an accurate approximation to $V_{xc}(\mathbf{r})$ using the

Chandrasekhar variational wave function as basis. Utilising this in Equation (15) allows an estimate of $E_{xc} + T_c$.

Additionally, there is an accurate knowledge of the form of the kinetic correlation energy density $t_c(\mathbf{r})$ introduced in Equation (16), but now, for non-relativistic He-like ions in the limit of large atomic number Z [11].

$$t_c(r) = -t_W(r) - \frac{1}{2} Z^2 n^2(r) - \frac{1}{2} Z \frac{\mathrm{d}n(r)}{\mathrm{d}r}, \tag{18}$$

where

$$t_W(r) = \frac{1}{8n(r)} \left(\frac{\mathrm{d}n(r)}{\mathrm{d}r} \right)^2 \tag{19}$$

is the Weizsäcker kinetic energy density.

4. Summary and future directions

The basic idea of the present study is to avoid iterative solution for the exchange-only potential $V_x(\mathbf{r})$ of DFT in the integral (Equation (6)). This is achieved, approximately, by utilising Equation (8), with $S(\mathbf{r})$ given in Equation (6). Finally, in Section 3 an approximation to include correlation is proposed.

As to future directions, it would already be of considerable interest if, for the two-electron He-like non-relativistic atomic ions with nuclear charge Ze, the formally exact asymptotic relation for large Z quoted in Equation (18), from [11] could be generalised to apply even to the case $Z = 2$ corresponding, of course, to the neutral He atom. Furthermore, the iterative solution of Equation (6) carried out by Howard and March [12] should be enriched by adding correlation effects (cf. Section 3).

Acknowledgements

Á. Nagy acknowledges grant OTKA No. K 67923.

References

[1] M. Levy and J.P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[2] Á. Nagy and N.H. March, Phys. Chem. Liquids **37**, 671 (1999).
[3] J.C. Slater, Phys. Rev. **81**, 385 (1951).
[4] P.A.M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930).
[5] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).
[6] O.V. Gritsenko and E.J. Baerends, Phys. Rev. A **64**, 042506 (2001).
[7] I.A. Howard and N.H. March, J. Chem. Phys. **119**, 5789 (2003).
[8] D.P. Joubert, Phys. Rev. A **76**, 042503 (2007).
[9] A. Solomatin, V. Sahni, and N.H. March, Phys. Rev. B **49**, 16856 (1994).
[10] F. Bogár, F. Bartha, and N.H. March, Phys. Rev. A **79**, 014501 (2009).
[11] T. Gál, N.H. March, and Á. Nagy, Chem. Phys. Lett. **305**, 429 (1999).
[12] I.A. Howard and N.H. March, Mol. Phys. **103**, 1261 (2005).