The key role of electron-nuclear potential energy in determining the ground-state energy of inhomogeneous electron liquids in both real and model atoms

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Abstract

Recent DFT work of Gál and March (GM) on the ground-state energy E of a two-electron model atom (like He, but with inverse square law interparticle repulsion) related E to the electron-nuclear potential energy U_{en} by $E = (1/2)U_{en}$. Also the model of GM satisfies $E = 2U_{en}$, but now with harmonic confinement. While modern non-relativistic DFT requires numerical treatment of real atoms, in the exact limit of DFT at large Z, the Thomas-Fermi theory is regained, where much analytical work can be done. This yields, as $Z \to \infty$, the non-relativistic energy of such neutral atoms as $E = (3/7)U_{en}$. The correlated electron density $\rho(r)$ is finally considered briefly in the two models cited above.

Keywords:Inhomogeneous electron liquids. Coulomb confinement. Two and four electron model atoms.

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1 Introduction

Only recently, through the study of Gál and March (GM below) [1], one of us (NHM) showed it was possible to give an exact model example of DFT [2], for the case of a two-electron spin-compensated model atom. In particular, writing the ground-state energy E as [2]

$$E = F[\rho] + \int \rho(r)V_{ext}(r)d\mathbf{r} \qquad (1)$$

GM have expressed F explicitly in terms of the exact ground-state density $\rho(r)$. This density is already known from the work of Capuzzi et al [3] to satisfy a linear homogeneous second-order equation for the model of Crandall et al [4] which was considered by GM. As follows from eqns (18) and (19) of [1], on the minimum one has the simple result that $F = E/2$. We note here that inserting this equality into eqn(1) above we are led immediately to the exact result that

$$E = 2 \int \rho(r)V_{ext}(r)d\mathbf{r} = 2U_{en} \ . \qquad (2)$$

However, in GM, though concerned dominantly with harmonic confinement characterized by $V_{ext} = (1/2)kr^2$, together with interparticle energy $u(r_{12}) = \lambda/r_{12}^2$, a generalization of the useful virial theorem was presented in the form of their eqn(7). GM stressed that provided one retained $u(r_{12})$ in the inverse square law form cited above, their eqn(7), which reads explicitly

$$F = \frac{1}{2} \int \rho(r)r\frac{\partial V_{ext}(r)}{\partial r}d\mathbf{r} \qquad (3)$$

with F as in eqn(1) above, was 'universal' in that it is valid for any external potential. Thus, for Coulomb confinement, with external potential given by

$$V_{ext}(r) = -\frac{Ze^2}{r} \qquad (4)$$

as in He-like ions with nuclear charge Ze, one readily finds from eqns (3) and (4) that

$$F = \frac{1}{2} \int \rho(r)\frac{Ze^2}{r}d\mathbf{r} = -\frac{1}{2}U_{en} \ , \qquad (5)$$

with U_{en} the electron-nuclear potential energy thereby defined for this different model atom. Inserting eqn (5) into eqn (1) we find immediately that

$$E = \frac{1}{2}U_{en} \qquad (6)$$

and hence $E = -F$ in this second model.

2   Theory of generalized virial theorem for power low models.

Real and most commonly studied model atoms show confinement and interparticle potential energies described by power or inverse power laws. In Table 1, we report the cases most widely studied from the literature. If we take an "atom" in which the external confining potential is proportional to a given power n of the distance from the center (the "nucleus") and in which the "electrons" are subjected to an interaction potential energy proportional to a power m of the interparticle distance, the virial theorem lead us to the following important relation

$$2T = nU_{en} + mU_{ee} \qquad (7)$$

where T is the kinetic energy, U_{en} the electron-nuclear potential energy and U_{ee} is the electron repulsion potential energy. By combining this relation with the definition of the total electronic energy, namely,

$$E = T + U_{en} + U_{ee} , \qquad (8)$$

and of the Hohenberg-Kohn functional F, namely,

$$F = T + U_{ee} \qquad (9)$$

we can easily obtain a system of two equations relating U_{en} and U_{ee} to E and F

$$
\begin{aligned}
E &= \left(1 + \tfrac{n}{2}\right) U_{en} + \left(1 + \tfrac{m}{2}\right) U_{ee} \\
F &= \tfrac{n}{2} U_{en} + \left(1 + \tfrac{m}{2}\right) U_{ee} .
\end{aligned}
\qquad (10)
$$

When $m = -2$ as in the Crandall et al [4] and GM [1] models, we recover the results recorded in the Introduction.

Model	n	m
Moshinsky [5]	2	2
Crandall et al [4]	2	–2
Hooke [6]	2	–1
Real atoms	–1	–1

Table 1: Exponents for the distances in confining (n) and interparticle interaction (m) potentials for real and some model atoms.

Now, it is interesting, instead, to move from these model systems to real atoms by switching to the interparticle interaction with Coulomb repulsion. In particular, we will consider harmonic (Hookean atoms) and Coulomb (real atoms) confinements.

2.1 Hookean atoms

The definition of Hookean atom goes back at least to Kestner and Sinanoglu [7] and corresponds to a harmonic external potential. In the case of such a confinement, it is possible to study the whole interval of confinement strength between the two limits of the external weak trap (Wigner regime) and of the strong confinement. In the Wigner regime, the kinetic energy is very small. If we take the limit when the kinetic energy $T \to 0$, the above system of equations (10) leads, using Table 1, to

$$
\begin{aligned}
E &= \left(1 - \tfrac{n}{m}\right) U_{en} = 3U_{en} \\
F &= -\tfrac{n}{m} U_{en} = 2U_{en}
\end{aligned}
\tag{11}
$$

Thus again we relate directly the external potential energy to the total electronic energy E and the HK functional F, as in the examples given in the Introduction. In the opposite regime of strong confinement, we can achieve a similar result by putting U_{ee}/U_{en} very small, U_{en} being dominant. In such case, in the limit $U_{ee}/U_{en} \to 0$, we obtain from eqn (10) that

$$
\begin{aligned}
E &= \left(1 + \tfrac{n}{2}\right) U_{en} = 2U_{en} \\
F &= \tfrac{n}{2} U_{en} = U_{en}
\end{aligned}
\tag{12}
$$

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As an illustrative example, we report in Figure 1 the ratio between E and U_{en} calculated for four electrons in a quintet ^5S_u state as a function of the frequency ω, the harmonic confining potential being $(1/2)\omega^2 r^2$ in atomic units. This plot shows two curves entirely comprised between the values of 2 and 3 and referring to diffusion Monte Carlo (DMC) calculations, performed in the Wigner regime [8], and unrestricted Hartree-Fock calculations made in the opposite regime of strong confinement.

The results above are independent on the number of electrons and we can state, as also shown in Figure 1, that

$$3U_{en} \geq E \geq 2U_{en} \ . \tag{13}$$

2.2 Real atoms and Thomas-Fermi theory

In contrast to Section 2.1, real atoms with spherical densities, such as He, Be or Ne, have a density $\rho(r)$ falling off monotonically from the value, ρ_0 say, at the nucleus and there is no Wigner limit. With strong confinement we have instead, from eqn (10),

$$2E \geq U_{en} \ . \tag{14}$$

In this regime, we have already presented results in previous work on Be-like ions [9].

2.2.1 Thomas-Fermi limit of heavy atoms and positive ions

Let us next make a comparison of the result (6), for harmonic confinement, with non-relativistic DFT for heavy neutral atoms. The ground-state energy is then given correctly, as Milne [10] first proposed in very early work, by the Thomas-Fermi [11] result, in atomic units,

$$E = -0.77Z^{7/3} \ . \tag{15}$$

Employing the virial theorem in the form $T = -E$ and the fact that $U_{ee} = (1/2) \int d\mathbf{r}_1 \mathbf{r}_2 \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/r_{12}$ is given by

$$U_{ee} = -\frac{1}{7}U_{en} \tag{16}$$

one can write

$$2E^{TF} = U_{en}^{TF} + U_{ee}^{TF} \tag{17}$$

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where the virial theorem, valid in TF theory, has been utilized. Hence it follows from eqns (16) and (17) that

$$E^{TF} = \frac{3}{7}U_{en} , \qquad (18)$$

which is to be compared with the model results given above. The above result (18) is valid for neutral atoms only, for which, in the Thomas-Fermi limit, the chemical potential μ is zero. For positive ions, eqn (18) generalizes to

$$E^{TF}(Z, N) = \frac{3}{7}\left[U_{en}(Z, N) + N\mu^{TF}(Z, N)\right] , \qquad (19)$$

as discussed, for example, in [12].

Eqn (19) relates E to $N\mu$ and U_{en} in the non-relativistic Thomas-Fermi limit of large Z and N for positive ions. This prompts us to add below a formally exact relation of this kind in DFT. The Euler equation of DFT reads, by minimizing $E - N\mu$ with respect to $\rho(\mathbf{r})$,

$$\mu = \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} + V_{ext}(\mathbf{r}) . \qquad (20)$$

Multiplying eqn (20) by $\rho(\mathbf{r})$ and then integrating through the whole space, one finds

$$N\mu = \int \rho(\mathbf{r})\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r} + U_{en} . \qquad (21)$$

Adding this eqn (21) to eqn (1) yields the formally exact result that

$$E + N\mu = F + \int \rho(\mathbf{r})\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r} + 2U_{en} . \qquad (22)$$

Finally, recognizing that eqn (19) gives eqn (18) above for $N = Z$ ($\mu^{TF} = 0$), we note that there is a relevance with real atoms at a critical atomic number Z_{cr} for which $IP = 0$. In Figure 2 we show a plot taken from data referring to our previous work on Be-like ions [9] to illustrate this particular behavior.

3 Conclusions

The main results of the present article consist in relating the electron-nuclear potential energy U_{en} to the ground-state energy E for both real and model atoms. For two models, both with just two electrons and different external potentials but the same inverse square law 'electron-electron' repulsion, eqns (2) and (6) relate U_{en} directly to E. Eqn (6) for Coulomb confinement has some resemblance to the Thomas-Fermi limit for real atoms in eqn (18). Finally, for Hookean atoms, we show that the total energy E is always comprised between the two limiting cases $3U_{en}$ and $2U_{en}$ in going from the Wigner regime to the regime of very strong confinement.

References

[1] Gál T, March NH. J Phys B At Mol Opt Phys. 2009; 42: 025001.

[2] Parr RG, Yang W. Density Functional Theory of Atoms and Molecules. New York: Oxford University Press; 1989.

[3] Capuzzi P, March NH, Tosi MP. J Phys A Math Gen. 2005; 38: L439.

[4] Crandall R, Whitnell R, Bettega R. Am J Phys. 1984; 52: 438.

[5] Moshinsky M. Am J Phys. 1968; 36: 52.

[6] Kais S, Herschbach DR, Handy NC. J Chem Phys. 1993; 99: 417.

[7] Kestner NR, Sinanoglu O. Phys Rev. 1962; 128: 2687.

[8] Amovilli C, March NH. Phys Rev A. 2011; 83: 044502.

[9] Amovilli C, March NH, Talman JD. Phys Rev A. 2008; 77: 032503.

[10] Milne EA. Proc Camb Phil Soc. 1927; 23: 794.

[11] March NH. Electron Density Theory of Atoms and Molecules. New York: Academic Press; 1993.

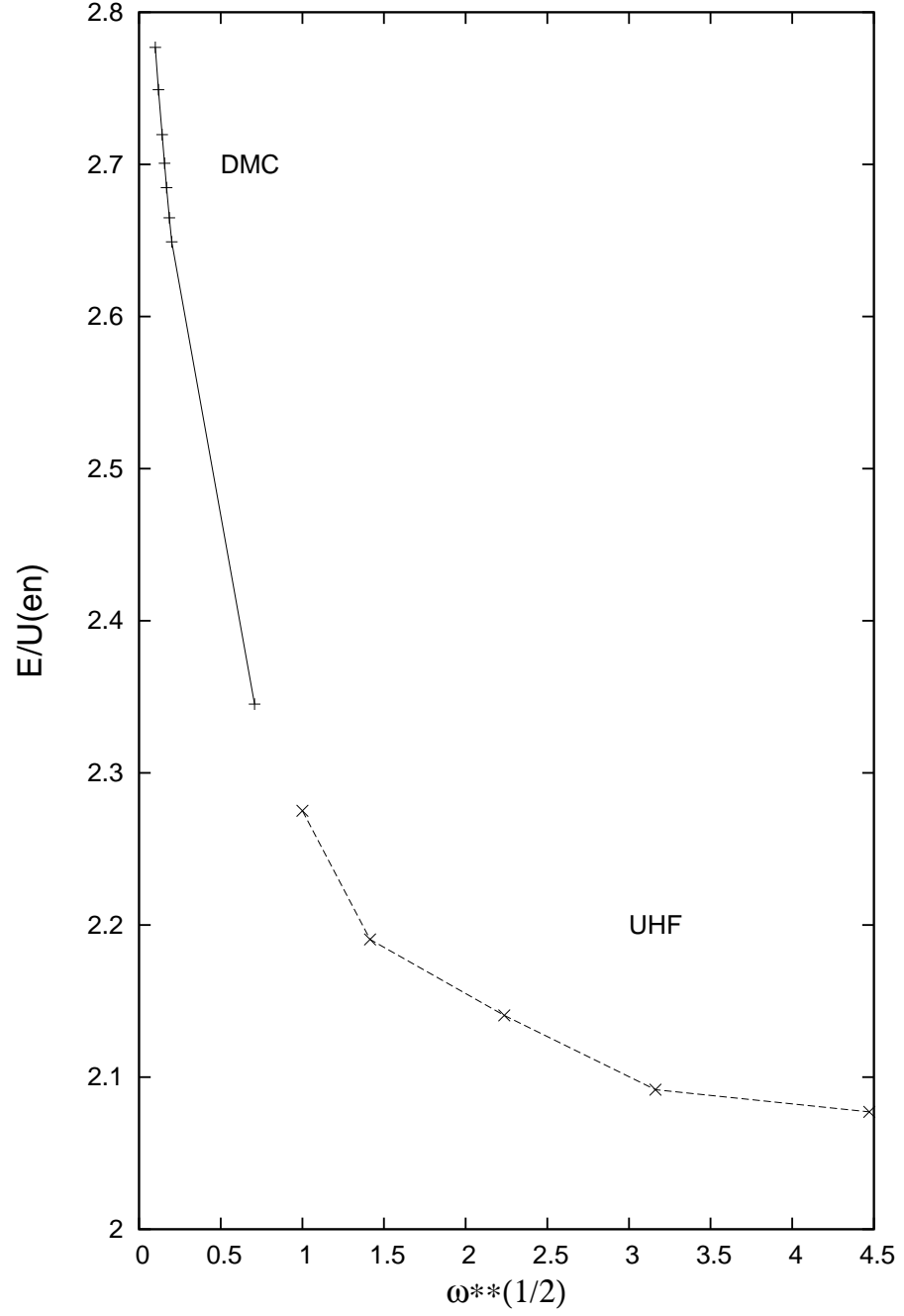[12] Kryachko ES, Ludena EV. Energy Density Functional Theory of Many-Electron Systems. Dordrecht: Kluwer; 1990.

Figure 1: E/U_{en} ratio, calculated at DMC level in the Wigner regime and at UHF level for strong confinement, against the square root of ω for a Hookean atom with four electrons in the ${}^5S_u$ state. Data are in a.u.
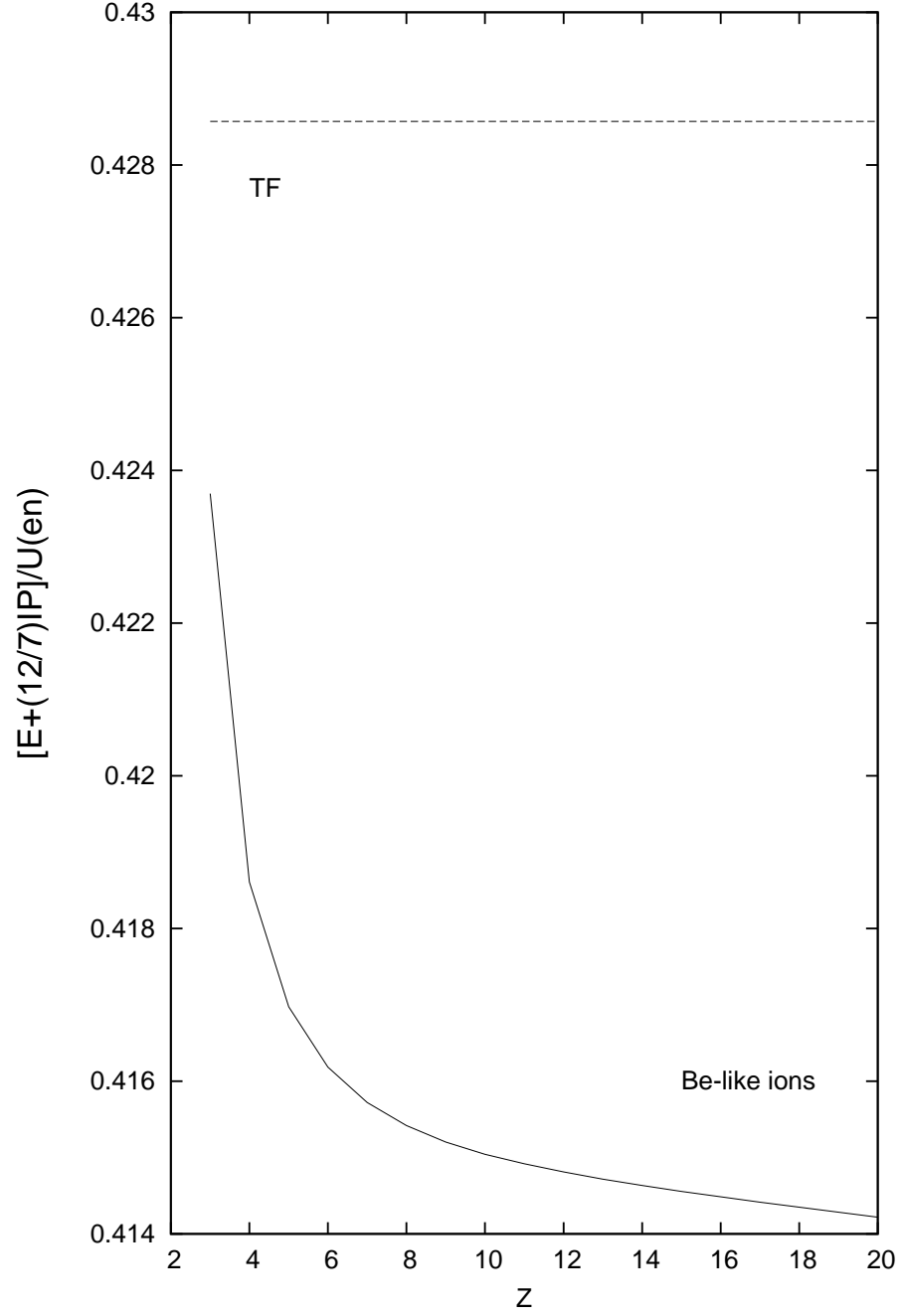
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Figure 2: Deviation from the Thomas-Fermi (TF) limit of Be-like ions ($N = 4$) in approaching the critical atomic number ($Z_c < 3$) following eqn (19) (see text). Data are in a.u.