

Exact integral constraint requiring only the ground-state electron density as input on the exchange-correlation force $-\partial V_{xc}(r)/\partial r$ for spherical atoms

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(October 2, 2008)

Abstract

Following some studies of $\int n(\mathbf{r})\nabla V(\mathbf{r})d\mathbf{r}$ by earlier workers for the DFT one-body potential $V(\mathbf{r})$ generating the exact ground-state density, we consider here the special case of spherical atoms. The starting point is the differential virial theorem, which is used, as well as the Hiller-Sucher-Feinberg identity to show, that the scalar quantity paralleling the above vector integral, namely $\int n(r)\partial V(r)/\partial r d\mathbf{r}$ is determined solely by the electron density $n(0)$ at the nucleus for the s-like atoms He and Be. The force $-\partial V/\partial r$ is then related to the derivative of the exchange-correlation potential $V_{xc}(r)$, by terms involving only the external potential in addition to $n(r)$. The resulting integral constraint should allow some test of the quality of currently used forms of $V_{xc}(r)$. The article concludes with results from the differential virial theorem and the Hiller-Sucher-Feinberg identity for exact many-electron theory of spherical atoms, as well as for DFT for atoms such as Ne with a closed p shell.

I. INTRODUCTION

The basic aim of this study is to derive new constraints on the exchange-correlation potential in density functional theory [1]. This field has a fairly long history, but it is still active. As a referee has pointed out to us, it is arguably more important now than in the past. This is due to the renewed interest in optimized-effective potential methods, as well as in other orbital-based functionals, where not only the energy, but also the potential are presently missing quantities.

To derive one of our central results given in Eq. (9) below, however, we have first had to limit the scope of our investigation to He and Be atoms. To generalize the present results to He- and Be-like ions is an elementary matter requiring change only in the external potential. This generalization to the entire (non-relativistic) 2- and 4-electron isoelectronic atomic series has the merit that it permits one to capture the different type of behavior for the correlation energy (and presumably also the correlation potential) in the limit as the atomic number Z tends to infinity.

II. FORCE-BALANCE AND DIFFERENTIAL VIRIAL EQUATIONS

One of us [2] has fairly recently written the force $-\partial V/\partial \mathbf{r}$ associated with the one-body potential $V(r)$ of DFT [1] for spherical atoms having ground-state density $n(r)$ in the form

$$-\frac{\partial V(r)}{\partial r} = -\frac{\partial V_{ext}(r)}{\partial r} + \frac{Q(r)}{r^2} - \frac{\partial V_{xc}(r)}{\partial r}, \quad (1)$$

where Gauss' theorem has been employed to introduce the number of electrons $Q(r)$ inside a sphere of radius r centered on the nucleus. Thus $Q(r)$ is explicitly

$$Q(r) = \int_0^r 4\pi s^2 n(s) ds. \quad (2)$$

Some workers have already made a study of the force $-\nabla V(\mathbf{r})$, which averages to zero. Below we consider the scalar analogue $-\int n(r)\partial V/\partial r d\mathbf{r}$ for especially He and Be atoms [3,4]. Our main focus here however is on the exchange-correlation force average $\langle F_{xc} \rangle$, defined by

$$\langle F_{xc} \rangle = - \int n(r) \frac{\partial V_{xc}(r)}{\partial r} d\mathbf{r}, \quad (3)$$

which is clearly related to $\langle F \rangle$ defined above by utilizing Eq. (1). Thus, if we multiply Eq. (1) throughout by $n(r)$, we find immediately, in an obvious notation:

$$\langle F_{xc} \rangle = \langle F \rangle - \langle F_{ext} \rangle - \int \frac{n(r)Q(r)}{r^2} d\mathbf{r}. \quad (4)$$

This Eq. (4) shows that given the external potential $V_{ext}(r) = -Z/r$, where Z is the atomic number of the spherical atom under consideration, and the ground-state density $n(r)$, the last two terms are readily evaluated. Thus the main task below is to evaluate $\langle F \rangle$ from knowledge of $-\partial V/\partial \mathbf{r}$ and $n(r)$. To proceed, we appeal to the differential virial theorem (DVT), going back to March and Young [5] in one dimension and generalized first to spherically symmetric systems by Nagy and March [6]: then to three dimensions by Holas and March [7]. In the form appropriate to DFT, the DVT reads

$$-\frac{\partial V}{\partial r} = -\frac{1}{4} \frac{\partial}{\partial r} \frac{\nabla^2 n(r)}{n(r)} + \frac{\hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r})}{n(r)}. \quad (5)$$

Here $\hat{\mathbf{r}}$ denotes the radial unit vector, while the vector field $\mathbf{z}^{(s)}(\mathbf{r})$ is defined via the kinetic energy density tensor $t_{\alpha\beta}^{(s)}(\mathbf{r})$ as [7]

$$t_{\alpha\beta}(\mathbf{r}) = \frac{1}{4} \left[\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} \gamma(\mathbf{r}', \mathbf{r}'') + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha} \gamma(\mathbf{r}', \mathbf{r}'') \right]_{\mathbf{r}''=\mathbf{r}'=\mathbf{r}}, \quad (6)$$

and the α component of the vector $\mathbf{z}(\mathbf{r})$ is given by

$$z_\alpha(\mathbf{r}) = 2 \sum_\beta \frac{\partial t_{\alpha\beta}(\mathbf{r})}{\partial r_\beta}. \quad (7)$$

In Eqs. (6) and (7), $\gamma(\mathbf{r}', \mathbf{r}'')$ is, as written the correlated one-particle density matrix. For DFT as a single-particle theory, γ goes to the Dirac density matrix [9] $\gamma^{(s)}(\mathbf{r}', \mathbf{r}'')$ generated by the one-body potential $V(r)$.

The next step is to use Eq. (5) to calculate the force $\langle F \rangle$ involving $-\partial V/\partial \mathbf{r}$ as

$$\langle F \rangle = - \int n(r) \frac{\partial V(r)}{\partial r} d\mathbf{r} = -\frac{1}{4} \int \frac{\partial}{\partial r} \nabla^2 n(r) d\mathbf{r} + \int \hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) d\mathbf{r}. \quad (8)$$

From Eq. (7) the single-particle counterpart is $\mathbf{z}_{s,\alpha}(\mathbf{r})$ and inserting this in the final integral appearing in Eq. (8) yields the value zero for He and for Be. For He this is because Akbari, March and Rubio [10] have shown that $\hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) = 4\frac{t_w(r)}{r} + 2\frac{\partial t_w(r)}{\partial r}$, where $t_w(r)$ is the von Weizsäcker kinetic energy density [18] and taking the volume integral of this latter quantity, and using the fact that $t_w(r) = \frac{1}{8} \frac{(n')^2}{n}$ vanishes at infinity, integration shows that $\int \hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) d\mathbf{r} = 0$ for the He atom. For Be also, in our own earlier work [11], we have shown that $\hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r})$ is obtained by replacing $t_w(r)$ by the positive definite gradient (G) kinetic energy $t_G(r)$. Again the volume integral $\int \hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) d\mathbf{r} = 0$, without full knowledge of $t_G(r)$, but only that it tends to zero at infinity.

The remaining quantity entering Eq. (8) involving the Laplacian $\nabla^2 n = n'' + (2/r)n'$ can be integrated by parts, the result being a known constant times the ground-state density at the nucleus, $n(r=0) \equiv n(0)$. Thus inserting the above integral on the left-hand-side of Eq. (8) into Eq. (1) we find

$$\langle F_{xc} \rangle = - \int n(r) \frac{\partial V_{xc}(r)}{\partial r} dr = -2\pi n(0) + 4\pi Z \int_0^\infty n(r) dr + 4\pi \int_0^\infty n(r) Q(r) dr. \quad (9)$$

This Eq. (9) applying to the spherical atoms He and Be is one of the central results of this article. It affords an integral constraint that should, whenever possible, be imposed on a chosen $V_{xc}(r)$, using the density $n(r)$ thereby generated in DFT. As is clear from Eq. (9), this density $n(r)$ is the only input needed to evaluate the right-hand-side of Eq. (9).

III. SOME MANY-ELECTRON GENERALIZATIONS

It seemed of interest to note here, prompted by the appearance of $\langle F_{ext} \rangle$ in Eq. (4), another form of DVT, but now in many-electron form [7]. Thus, we can write

$$-\frac{\partial V_{ext}}{\partial r} = -\frac{1}{4} \frac{\frac{\partial}{\partial r} \nabla^2 n(r)}{n(r)} + \frac{\hat{\mathbf{r}} \cdot \mathbf{z}(\mathbf{r})}{n(r)} + \hat{\mathbf{r}} \cdot \mathbf{F}_{ee}(\mathbf{r}), \quad (10)$$

where the many-electron vector field $\mathbf{z}(\mathbf{r})$ has already been defined in Eqs. (6) and (7). Forming $\langle F_{ext} \rangle$ from Eq. (10) we find

$$\langle F_{ext} \rangle = - \int n(r) \frac{\partial V_{ext}(r)}{\partial r} d\mathbf{r} = -2\pi n(0) + \int \hat{\mathbf{r}} \cdot \mathbf{z}(\mathbf{r}) d\mathbf{r} + \int n(r) \hat{\mathbf{r}} \cdot \mathbf{F}_{ee}(\mathbf{r}) d\mathbf{r}. \quad (11)$$

In the Abstract, we referred to the Hiller-Sucher-Feinberg identity [12,13]. Briefly, this can be regarded as derivable, in the single-particle case of DFT from the appropriate one-electron Schrödinger equations [14]

$$\nabla^2 \psi_i + 2 [\varepsilon_i - V(r)] \psi_i = 0. \quad (12)$$

For, say, the Ne atom, with configuration $(1s)^2(2s)^2(2p)^6$ we need to write the separable form

$$\psi_i(r) = R_i(r) Y_{lm}(\theta, \phi) \quad (13)$$

and with $P_i(r) = rR_i(r)$ we find

$$\frac{d^2 P_i}{dr^2} + 2 \left[\varepsilon_i - V(r) - \frac{l_i(l_i + 1)}{2r^2} \right] P_i = 0. \quad (14)$$

Dividing both sides by P_i and then differentiating with respect to r , we find the combination $-\partial V/\partial r + l(l+1)/r^3$ which enters the HSF identity as in the generalized single-particle form given by Katriel [15]. The one-particle result is then found as

$$2\pi n_i(0) = \langle \psi_i | \frac{\partial V(r)}{\partial r} - \frac{\hat{l}_i^2}{r^3} | \psi_i \rangle, \quad (15)$$

where \hat{l}_i^2 is the appropriate angular momentum operator yielding the last term on the RHS of Eq. (15) and n_i is the one-particle density. After summing for the occupied orbitals Eq. (15) leads to the non-interacting result

$$2\pi n(0) = \int n(r) \frac{\partial V(r)}{\partial r} d\mathbf{r} - \sum_i \lambda_i \int \frac{l_i(l_i + 1)}{r^3} n_i(r) d\mathbf{r}, \quad (16)$$

where λ_i are the occupation numbers.

Returning to Eq. (5), direct comparison with Eq. (16) allows us to write

$$\int \hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) d\mathbf{r} = - \sum_i \lambda_i \int n_i(r) \frac{l_i(l_i + 1)}{r^3} d\mathbf{r} \quad (17)$$

We see immediately why, when we move from He and Be to Ne, the last atom having a closed $(2p)^6$ shell, the above integral on the left-hand-side of Eq. (17) is no longer zero. Eq. (17) is a further important result of the present investigation.

In fact, in an earlier study [10], we have shown quite generally for spherical atoms that

$$\hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r}) = 4\frac{t_w}{r} + 2t'_w + n(r)V'_P(r), \quad (18)$$

where $V_P(r)$ is the Pauli potential. For Be we know that $\int \hat{\mathbf{r}} \cdot \mathbf{z}^{(s)}(\mathbf{r})d\mathbf{r} = 0$, as well as the first term on the right-hand-side of Eq. (18) having zero volume integral, it then follows for Be that $\int n(r)V'_P(r)d\mathbf{r} = 0$. This cannot continue to hold when Ne with its $(2p)^6$ shell is considered, since the \hat{l}^2 term in Eq. (17) is obviously no longer zero.

Paralleling the many-electron form of the DVT in Eq. (10), it is next to be noted that the analogue of the single-particle HSF identity (16) is given in [12,13] as follows.

Specifically for the many-electron ground-state wave function $\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N)$ of the N -electron spin-free Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + W, \quad (19)$$

where

$$W = \sum_{i=1}^N V_{ext}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{r_{ij}}, \quad (20)$$

the HSF identity takes the form

$$2\pi n(0) = \langle \Psi | \frac{\partial W}{\partial r_1} - \frac{\hat{L}_1^2}{r_1^3} | \Psi \rangle. \quad (21)$$

In Eq. (21) $r_1 = |\mathbf{r}_1|$, $\hat{L}_1 = -i\mathbf{r}_1 \times \nabla_1$ are written in terms of the spatial coordinate \mathbf{r}_1 .

To make contact with the corresponding DVT Eq. (11), let us take again the case of the He atom. Eq. (21) has been evaluated recently by Amovilli and March [16] for Ψ_c replaced by the variational wave function $\Psi(r_1, r_2, r_{12})$ of Chandrasekhar [17], where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. However, Eq. (4) of [16] remains true when Ψ is replaced by the (as yet unknown) exact $\Psi(r_1, r_2, r_{12})$ for the ground state of He. No contribution, of course, in this simple example, comes from the angular momentum term in Eq. (21), the result being

$$2\pi n(0) = \int d\mathbf{r}_1 d\mathbf{r}_2 \Psi^2(r_1, r_2, r_{12}) \left[Z \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - \frac{1}{r_{12}^3} \left(\frac{r_1^2 - \mathbf{r}_1 \cdot \mathbf{r}_2}{r_1} + \frac{r_2^2 - \mathbf{r}_1 \cdot \mathbf{r}_2}{r_2} \right) \right]. \quad (22)$$

Noting that the pair density $n_2(\mathbf{r}_1, \mathbf{r}_2) = 2\Psi^2(\mathbf{r}_1, \mathbf{r}_2)$, one can finally bring Eq. (20) into contact with the many-electron DVT result (11) since $\mathbf{F}_{ee}(\mathbf{r})$ appearing there has the form

$$\mathbf{F}_{ee}(\mathbf{r}) = \frac{2}{n(\mathbf{r})} \int d\mathbf{r}' n_2(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (23)$$

In Eq. (23), the atomic number Z has been retained in the external potential terms, Z being of course equal to 2 for the neutral atom. Manipulation of Eq. (23), when inserted into (11) gives back $n(0)$ as in Eq. (22).

IV. SUMMARY AND PROPOSED FUTURE DIRECTIONS

A central result of the present investigation is embodied in Eq. (9). This gives an exact integral constraint on the exchange-correlation force $-\partial V_{xc}/\partial r$ in terms solely of the ground-state density. For the He atom, this is in principle available by X-ray scattering from the vapor, though high experimental accuracy will be required to extract, via the X-ray scattering factor

$$F(k) = \int n(r) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}, \quad (24)$$

the ground-state density $n(r)$. Such a procedure has been studied recently by Van Alsenoy and March [19,20] in the context of the neon atom and an 'almost spherical' molecule like methane. But to our knowledge, only very old measurements available, in principle, to extract $F(k)$ for He atom, and going back to the early days of quantum mechanics exist for He vapor. As for Be, some 50 Bragg reflection intensities have been measured by Brown [21] (see also [22]), but now one has itinerant electrons in the metallic crystal under investigation. However, for the Be atom quantum Monte Carlo data is now available for the ground-state density [23]. But even there, the accuracy available by current QMC techniques for the density $n(0)$ at the nucleus, which enters the constraint (9) derived here, leaves something to be desired.

A referee has asked us, in addition to Eq. (9) to emphasize that the 'fully many-electron' result (11) may also be a further significant equation in the future.

We have, of course, in considering He and Be, restricted ourselves to closed shells. Available spin-density functional theory allows one to treat general systems, which are not spin-compensated, such as the Li atom. Then the one-particle equations (14) take the form

$$\frac{d^2 P_{i\sigma}}{dr^2} + 2 \left[\varepsilon_{i\sigma} - V_{sigma}(r) - \frac{l_i(l_i + 1)}{2r^2} \right] P_{i\sigma} = 0, \quad (25)$$

where the subscript σ refers to the spin up or the spin down case. Then instead of Eq (16) we have two equations

$$2\pi n_\sigma(0) = \int n_\sigma(r) \frac{\partial V_{sigma}(r)}{\partial r} d\mathbf{r} - \sum_i \lambda_i \int \frac{l_i(l_i + 1)}{r^3} n_i(r) d\mathbf{r}, \quad (26)$$

where in the last term the sum is only for the occupied electrons with spin σ . That is, we have separate constraints for the spin up and the spin down potentials.

Also, in the future, variations in the external potential from bare Coulomb confinement, to say, ultracold Fermion atomic gases, which are essentially harmonically confined due to magnetic trapping techniques [24] are also of interest. For spin-compensated two-electron systems with spherical symmetry, and harmonic confinement with general effective interaction $u(r_{12})$ replacing $1/r_{12}$ in He, this problem has been completely solved by Holas, Howard and March [25]. But to date, the interesting generalization to Be-like 4-electron spin-compensated cases has not proved amenable to analytic solution. And, of course, generalizations to molecules like Li-H are of interest for the future, in again this four-electron case.

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ACKNOWLEDGMENTS

We wish to thank the two referees for both numerous specific comments, and for more general observations which are now reflected in the final, expanded manuscript, and in particular in section I and IV. NHM wishes to acknowledge that his contribution to the present study was brought to fruition during a visit to the University of Debrecen. NHM also thanks Professors D. Van Dyck and D. Lamoen for making possible his continuing affiliation with the University of Antwerp (UA) due to partial financial support from UA through the BOF-NOI. ÁN acknowledges grant OTKA No. T 67923.