

# Use of the differential virial theorem to estimate the spatial variation of the exchange-correlation force $-\partial V_{XC}(r)/\partial r$ in the ground states of the spherical atoms He and Be

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We use the differential virial theorem (DVT) directly to display the approximate spatial dependence of the exchange-correlation (XC) force in He and Be, applying an exact integral constraint on the XC force, recently established by March and Nagy. In He, an analytic ground-state density  $n(r)$ , combined with the DVT plus the von Weizsäcker single-particle kinetic energy, suffices to determine an approximate XC force. For Be, the XC force is calculated for the semiempirical fine-tuned Hartree-Fock density, as proposed by Cordero *et al.* [Phys. Rev. A **75**, 052502 (2007)]. However, for the single-particle kinetic energy, following Dawson and March, a phase  $\theta(r)$  must be obtained by solving numerically a nonlinear pendulumlike equation.

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## I. INTRODUCTION

Very recently, March and Nagy [1] have established an exact integral constraint on the exchange-correlation (XC) force  $f_{XC} = -\partial V_{XC}(r)/\partial r$  in the ground states of the spherical atoms He and Be, where  $V_{XC}(r)$  is the XC potential in current usage in density functional theory (DFT). As in [1], we take the differential virial theorem (DVT), going back to the work of March and Young [2] in one dimension and generalized to three dimensions by Holas and March [3] as a starting point. If  $V(r)$  is the customary one-body potential of DFT [4], the result in [3] for the DVT reads

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

In Eq. (1),  $n(r)$  denotes the ground-state density, while  $\mathbf{z}_s(\mathbf{r})$  is defined from the kinetic-energy density tensor  $t_{\alpha\beta}(\mathbf{r})$  given in [3] by its  $\alpha$  component having the form

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

Finally, in Eq. (1) written in the spherical symmetry appropriate for the He and Be,  $\hat{\mathbf{r}}$  denotes the unit radial vector  $\mathbf{r}/r$ .

Then multiplying Eq. (1) by  $n(r)$  and then integrating over the whole of space the result

$$\int n(r) \frac{\partial V(r)}{\partial r} d\mathbf{r} = 2\pi n(r=0) \quad (3)$$

was obtained in [1]. Equation (3) can be verified by considering the two contributing terms. The first one is

$$\int_\Omega \hat{\mathbf{r}} \cdot \nabla(\nabla^2 n) d\mathbf{r} = \oint_{\partial\Omega} \nabla^2 n \hat{\mathbf{r}} d\mathbf{F} - 2 \int_\Omega \frac{\nabla^2 n}{r} d\mathbf{r} \quad (4)$$

using Gauss' theorem for arbitrary  $n(\mathbf{r})$  ground-state atomic density. The surface integral goes to zero as  $\Omega \rightarrow \infty$ . Furthermore, it was derived in [5,6] that

$$\frac{1}{4\pi} \int \frac{\nabla^2 n(\mathbf{r})}{r} d\mathbf{r} = -n(\mathbf{0}). \quad (5)$$

As shown in [1] the second term in both He(1s)<sup>2</sup> and Be(1s)<sup>2</sup>(2s)<sup>2</sup> (*s*-type only orbitals) is

$$\hat{\mathbf{r}} \cdot \mathbf{z}_s(\mathbf{r}) = 4 \left[ \frac{t_G(r)}{r} + \frac{1}{2} \frac{\partial t_G(r)}{\partial r} \right], \quad (6)$$

where  $t_G(r)$  is the positive-definite gradient form of the single-particle kinetic energy. Using the fact that  $r^2 t_G \rightarrow 0$  for both  $r \rightarrow 0$  and  $r \rightarrow \infty$ , this integrates as

$$\int \hat{\mathbf{r}} \cdot \mathbf{z}_s(\mathbf{r}) d\mathbf{r} = 8\pi [r^2 t_G(r)]_{r=0}^\infty = 0. \quad (7)$$

## II. USE OF THE DVT EQUATIONS FOR THE He ATOM

Howard *et al.* calculated previously [7] the ground-state density  $n(r)$  analytically from the Chandrasekhar wave function [8]  $\Psi_C(r_1, r_2, r_{12})$ : namely,

$$\Psi_C \propto (1 + cr_{12})(e^{-ar_1 - br_2} + e^{-br_1 - ar_2}). \quad (8)$$

The best variational parameters  $a=1.436$ ,  $b=2.208$ , and  $c=0.2924$  were obtained by Green *et al.* [9]. Obviously, then, the density at the nucleus can be calculated as a limit as  $r \rightarrow 0$ , which is

$$n_C(r=0) = 3.540. \quad (9)$$

Clearly an approximation to the first term on the right-hand side of Eq. (1) is given by inserting  $n_C(r)$  in the place of  $n(r)$ . As for the final term,  $t_G(r)$  in Eq. (6) is simply the von Weizsäcker [10] kinetic energy  $t_W(r)$ , which in turn is given by

$$t_W(r) = \frac{\hbar^2}{8m} \frac{(\partial n / \partial r)^2}{n(r)}. \quad (10)$$

Again replacing  $n$  by  $n_C$ , we have an approximation to the final term in Eq. (1).

To extract the desired XC force, Gauss' theorem was used to write  $-\partial V(r)/\partial r$  in the DVT (1) as

$$-\frac{\partial V(r)}{\partial r} = -\frac{\partial V_{ext}}{\partial r} + \frac{e^2 Q(r)}{r^2} - \frac{\partial V_{XC}}{\partial r}. \quad (11)$$

Here,  $Q(r)$  is the number of electrons enclosed by a sphere of radius  $r$  centered on the nucleus:

$$Q(r) = \int_0^r 4\pi s^2 n(s) ds, \quad (12)$$

which can be evaluated [ $Q_C(r)$ , say] by inserting  $n_C(r)$  for  $n(r)$ . Finally in Eq. (11),  $V_{ext} = -Ze^2/r$ , where  $Z=2$  would be for He. However, the effective nuclear charge consistent with the density is determined by Kato's cusp condition [11]

$$\lim_{r \rightarrow 0} \frac{1}{n(r)} \frac{\partial n(r)}{\partial r} = -2Z_{Kato}. \quad (13)$$

For the  $n_C(r)$  with the Green's parameters, one finds  $Z_{Kato} = 1.963$ . Using this value, the divergent nuclear attraction term for small  $r$  is properly separated from the exchange

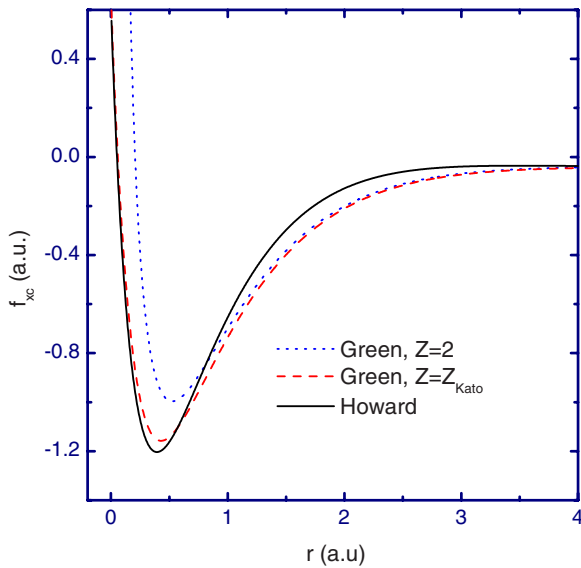


FIG. 1. (Color online) The exchange-correlation force  $f_{XC}$  for the He atom using the density obtained from the Chandrasekhar wave function. Blue, dotted line: Green's variational parameters and  $Z=2$ . Red, dashed line: Green's variational parameters and  $Z=1.963$  effective nuclear charge. Black, solid line: Howard's consistent parameters,  $Z=2$ .

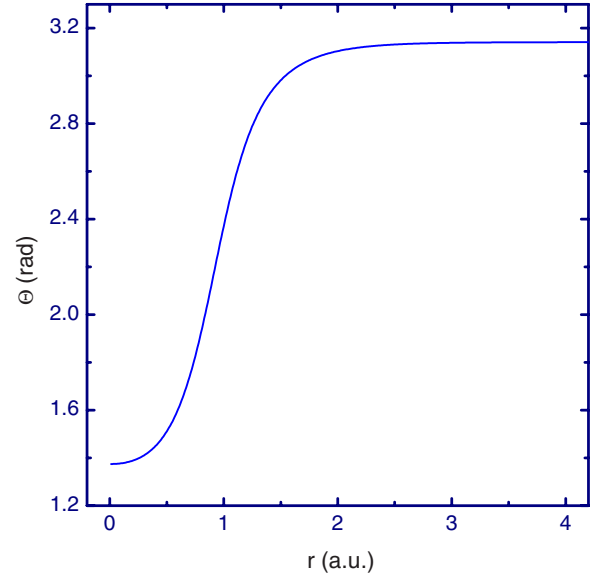


FIG. 2. (Color online) The phase factor  $\Theta(r)$  for the Be atom as the result of the numerical solution of the corresponding differential equation using the fine-tuned HF density.

force as shown in Fig. 1. The third curve in Fig. 1 shows also the XC force versus  $r$  for values of  $a$ ,  $b$ , and  $c$  in Eq. (8) using the consistent set ( $a=1.3449$ ,  $b=2.2605$ ,  $c=0.2385$ ) of Howard and March [12]. These parameters are close to the best variational ones, but most importantly they reproduce the He nuclear charge and the experimental ionization potential.

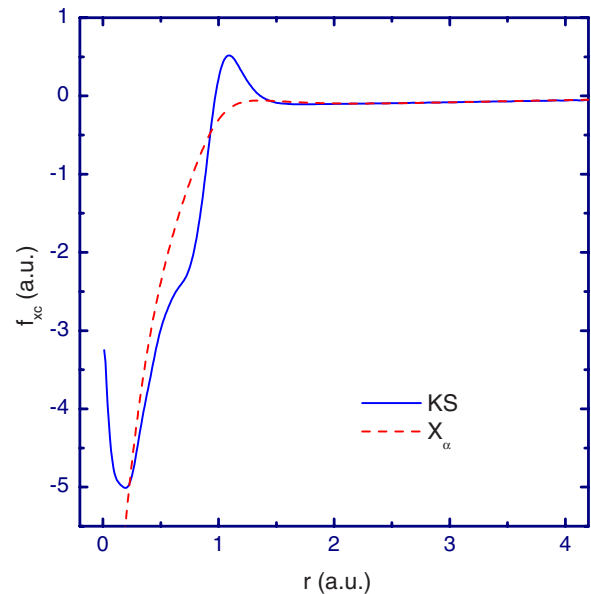


FIG. 3. (Color online) The exchange-correlation force  $f_{XC}$  for the Be atom from the fine-tuned HF density. Blue, solid line: the Kohn-Sham force from the force equation. Red, dashed line: the  $X_\alpha$  force with  $\alpha=0.7$  for comparison.

### III. EXCHANGE-CORRELATION FORCE FOR THE Be ATOM GROUND STATE

We have felt it best to adopt for  $n(r)$  for the Be atom the semiempirical fine-tuned Hartree-Fock (HF) result of Cordero *et al.* [13]. This involved solving the HF equations numerically for nonintegral nuclear charge (4.127, instead of  $Z=4$  [13]).

Returning to the DVT in Eq. (1), the first term on the right-hand side is determined by the semiempirical refinement of the HF density. The new feature for Be beyond the He atom case discussed above is that

$$t_G(r) = t_W + \frac{1}{2}n(r) \left[ \frac{\partial\theta(r)}{\partial r} \right]^2 \quad (14)$$

(see Dawson and March [14]) and  $\theta(r)$  is determined, as mentioned above, by the pendulumlike nonlinear equation

$$\nabla^2\theta(r) + \frac{\nabla n(r)}{n(r)} \cdot \nabla\theta(r) + \lambda \sin 2\theta = 0. \quad (15)$$

The parameter  $\lambda = \varepsilon_1 - \varepsilon_2$  is the difference between the unknown Kohn-Sham  $1s$  and  $2s$  orbital energies. During the numerical solution of the differential equation,  $\lambda$  is treated as an eigenvalue. Normalized one-electron wave functions

(nodeless  $1s$  and  $2s$  with one node) were found at  $\lambda = -4.117$ . In Fig. 2 the corresponding  $\theta(r)$  vs  $r$  is shown.

### IV. SUMMARY AND FUTURE DIRECTIONS

The main result of this Brief Report for the ground state of the He atom is the exchange-correlation force  $-\partial V_{XC}(r)/\partial r$  depicted in Fig. 1 for a few sets of parameters in the Chandrasekhar wave function (8).

For Be, we have no analytic counterpart for  $n_C(r)$  as in [7] for He, but only the tabulated semiempirical refinement of the HF density. The additional feature here is the numerical solution of the nonlinear eigenvalue problem posed by Eq. (15) when the Cordero density is inserted, leading to the phase  $\theta(r)$  shown in Fig. 2. The predicted form of the XC force in the ground state of the Be atom is finally displayed in Fig. 3.

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