

Nonlocal functional derivative of kinetic energy for the self-consistent Thomas-Fermi atom

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It is well known in the Thomas-Fermi (TF) theory that the functional derivative $\delta T/\delta n(r)$, with T the kinetic energy and $n(r)$ the ground-state electron density, is proportional to $n^{2/3}(r)$. But the differential equation satisfied by the TF self-consistent density for atoms is shown here to express $n^{1/3}(r)$ as a linear combination of $\nabla^2 n/n$ and $(\nabla n/n)^2$. Hence a nonlocal form for $\delta T/\delta n(r)$ follows, solely in terms of these two variables. [S1050-2947(97)00607-0]

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Current emphasis in density functional theory is being given to the role of functionals involving low-order derivatives of the ground-state electron density $n(r)$. For a single electron, the functional is known to be that given by von Weizsäcker [see Eq. (5) below]. However, one wants to deal with substantial numbers of electrons N in, say, atomic and molecular structure. Therefore, in this paper, we shall return to the original (statistical in concept, i.e., large N) Thomas-Fermi (TF) self-consistent theory of neutral atoms [1]. Below, we shall construct the explicit differential equation satisfied by the ‘‘universal’’ electron density of that method. Since the same reduced density gradient variables enter as in the von Weizsäcker case, and since also the result is simple, we will quote it at the outset and then prove it subsequently. It is

$$\frac{\nabla^2 n}{n} - \frac{1}{3} \left(\frac{\nabla n}{n} \right)^2 = \frac{n^{1/3}}{l}, \tag{1}$$

where the constant l , having the dimensions of length, will be obtained below. Given this result, entirely equivalent to the usual TF potential equation for atoms, one can rewrite the functional derivative of the kinetic energy $T = c_K \int n^{5/3} d\mathbf{r}$ of that theory [1], namely,

$$\frac{\delta T}{\delta n(r)} = \frac{5}{3} c_K n^{2/3}(r), \quad c_K = \frac{3h^2}{10m} \left(\frac{3}{8\pi} \right)^{2/3} \tag{2}$$

in terms of the two quantities $(\nabla^2 n/n)$ and $(\nabla n/n)^2$ appearing in Eq (1).

The desired result is then

$$\frac{\delta T}{\delta n(r)} = \frac{5}{3} c_K l^2 \left[\frac{\nabla^2 n}{n} - \frac{1}{3} \left(\frac{\nabla n}{n} \right)^2 \right]^2. \tag{3}$$

This explicit ‘‘nonlocal’’ form is expected to be asymptotically valid for heavy atoms treated solely by means of the nonrelativistic many-electron Schrödinger equation, i.e., in the limit for neutral atoms of large atomic number Z [2,3]. What is to be stressed at this point is that, though Eqs. (2) and (3) are identical, because of Eq. (1), the introduction of

the ‘‘reduced’’ density gradient variables gives greater flexibility in the construction of functionals for the intermediate numbers of electrons N met in atoms and molecules.

Returning to the single-electron case already referred to, in order to press this point further, for the H-like atom or the H_2^+ molecular ion, we have the elementary result that

$$\frac{\delta T}{\delta n(r)} = \frac{\delta T_W}{\delta n(r)}, \tag{4}$$

where T_W is the von Weizsäcker kinetic energy given by [4]

$$T_W = \frac{\hbar^2}{8m} \int \frac{(\nabla n)^2}{n} d\mathbf{r}. \tag{5}$$

Thus we find for the number of electrons $N=1$ the general result

$$\frac{\delta T}{\delta n(\mathbf{r})} = - \frac{\hbar^2}{4m} \left[\frac{\nabla^2 n}{n} - \frac{1}{2} \left(\frac{\nabla n}{n} \right)^2 \right]. \tag{6}$$

the same two variables characterizing both the limiting cases $N=1$ and large N from Eqs. (6) and (3). It naturally does not follow that the form

$$\frac{\delta T}{\delta n(r)} \doteq F \left(\frac{\nabla^2 n}{n}, \left(\frac{\nabla n}{n} \right)^2, N \right) \tag{7}$$

will still work well for an arbitrary number of electrons $N = \int n(r) d\mathbf{r}$ but it is clearly tempting to conjecture that it may well be a useful starting point for approximating the functional derivative of the kinetic energy. Whether the assumption (7) is powerful enough to reproduce shell structure in the atomic radial density $D(r) = 4\pi r^2 n(r)$ remains an outstanding question bearing on the approximate conjecture (7). But be that as it may, let us return to obtaining the length in Eq. (1) for the self-consistent TF atom.

Writing the self-consistent potential energy $V(r)$ in the customary form

$$V(r) = - \frac{Ze^2}{r} \phi(x), \tag{8}$$

the ‘‘screening function’’ $\phi(x)$ satisfies the differential equation

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$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}. \quad (9)$$

Here both ϕ and x are dimensionless, x being related to the radial distance r from the nucleus by [5]

$$r = bx = \alpha a_0 x / Z^{1/3}, \quad \alpha = (1/4)(9\pi^2/2)^{1/3}, \quad a_0 = \hbar^2/m e^2. \quad (10)$$

The density $n(r)$, on which we focus all attention below, is related to $V(r)$ for a neutral atom by the inhomogeneous electron-gas relations [1–3]

$$n(r) = \frac{8\pi}{3h^3} p_F(r)^3 \quad (11)$$

and

$$\mu = \frac{p_F^2(r)}{2m} + V(r). \quad (12)$$

For the neutral atom case taken here as the example throughout, the chemical potential μ is identically zero. Using Eq. (8) for $V(r)$, it follows that

$$n(r) = \frac{8\pi(2m)^{3/2}}{3h^3} \left(\frac{Z^{4/3} e^2 \phi}{\alpha a_0 x} \right)^{3/2} = AZ^2 \left(\frac{\phi}{x} \right)^{3/2}, \quad (13)$$

where Eq. (13) conveniently defines the constant A , which has dimensions of $(\text{length})^{-3}$. Thus, returning to Eq. (9) one finds

$$\frac{d^2\phi}{dx^2} = \frac{xn(r)}{AZ^2}. \quad (14)$$

But from Eq. (13) it follows that

$$\phi = (AZ^2)^{-2/3} xn^{2/3}(r) \quad (15)$$

and hence

$$\frac{d^2\phi}{dx^2} = \frac{2}{3} \frac{br}{(AZ^2)^{2/3}} n^{-1/3}(r) \left[\nabla^2 n - \frac{1}{3} \frac{(\nabla n)^2}{n} \right]. \quad (16)$$

Eliminating $d^2\phi/dx^2$ from Eq. (16) using Eq. (14) yields, after a little manipulation involving the constants b and A in Eqs. (10) and (13), respectively, Eq. (1) with the length l given explicitly as

$$l = \frac{1}{4} \left(\frac{\pi}{3} \right)^{1/3} a_0, \quad (17)$$

where a_0 is the Bohr radius defined in Eq. (10).

A check of Eq. (1) with l given by Eq. (17) is that ϕ in Eq. (9), for the neutral atom, tends to $144/x^3$ far from the nucleus [6] and this is in fact an exact solution of Eq. (9), but does not, of course, satisfy the physical boundary condition $\phi(0)=1$ required by Eq. (8) at the point nucleus of charge Ze . From Eq. (13) it then follows that $n(r) = (12)^3 A \alpha^6 a_0^6 / r^6$ must be an exact mathematical solution of Eq. (1), with l given by Eq. (17). Substituting this solution in $\nabla^2 n/n$ gives $30/r^2$, for $(-1/3)(\nabla n/n)^2$ yields $-12/r^2$, while the right-hand side is readily confirmed from Eq. (17) to be $18/r^2$.

In summary, the self-consistent TF density $n(r)$ of heavy neutral atoms satisfies the differential equation (1), with the length l given by Eq. (17). Combining Eqs. (1) and (2), one is led to the nonlocal functional derivative $\delta T/\delta n(r)$ in Eq. (3). Just as for the exact result (6) for the one-electron problem, $\delta T/\delta n(r)$ in Eq. (3) depends only on the quantities $\nabla^2 n/n$ and $(\nabla n/n)^2$, which is encouraging for further studies of the kinetic energy functional. More speculatively, we could add exchange in the spirit of Scott [7], who calculated the Dirac-Slater form of exchange [8], but still retaining the original TF density $n(r)$. Then Eq. (1) essentially expresses the Dirac-Slater $n^{1/3}(r)$ exchange potential [9] linearly in terms of $(\nabla^2 n/n)$ and $(\nabla n/n)^2$. But, of course, additional approximations are now invoked beyond those made in determining the functional derivative $\delta T/\delta n(r)$ in Eq. (3).

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