

# Local density functional theory of atoms and molecules

(statistical theory/Thomas-Fermi method)

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**ABSTRACT** A local density functional theory of the ground electronic states of atoms and molecules is generated from three assumptions: (i) The energy functional is local. (ii) The chemical potential of a neutral atom is zero. (iii) The energy of a neutral atom of atomic number  $Z$  is  $-0.6127 Z^{7/3}$ . The energy functional is shown to have the form

$$E[\rho] = \frac{3}{5} A_0 \int \rho^{5/3} d\tau + \frac{3}{4} B_0 N^{2/3} \int \rho^{4/3} d\tau + \int v \rho d\tau$$

where  $A_0 = 6.4563$  and  $B_0 = 1.0058$ . The first term represents the electronic kinetic energy, the second term represents the electron-electron repulsion energy for  $N$  electrons, and the third term is the nucleus-electron attraction energy. The energy  $E$  and the electron density  $\rho$  are obtained and discussed in detail for atoms; their general properties are described for molecules. For any system the density becomes zero continuously at a finite distance from nuclei, and contours of the density are contours of the bare-nuclear potential  $v$ . For an atomic species of fractional charge  $q = 1 - (N/Z)$ , an energy formula is obtained,

$$-E/Z^2 N^{1/3} = 0.6343 + 0.1721q,$$

which fits Hartree-Fock energies of 625 atoms and ions with root-mean-square error of 0.0270. A more general local density functional involving a coefficient  $B(N) = B_0 N^{2/3} + B_1$  is briefly considered.

For the ground state of an atomic or molecular electronic system, Hohenberg and Kohn (1) have shown that there exists a stationary principle determining the spin-free electron density  $\rho = \rho(1) = N \int \dots \int |\psi|^2 d\omega_1 dx_2 \dots dx_N$  and the electronic energy  $E$ , having the form

$$\delta(E[\rho] - \mu N[\rho]) = 0. \quad [1]$$

Here  $N[\rho]$  is the functional determining the number of particles,

$$N[\rho] = \int \rho(1) d\tau_1, \quad [2]$$

the quantity  $\mu$  is the chemical potential of the system of interest, and the energy functional  $E[\rho]$  is a sum of three functionals,

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ne}[\rho], \quad [3]$$

where  $T[\rho]$  is the electronic kinetic energy,  $V_{ee}[\rho]$  is the electron-electron repulsion energy and  $V_{ne}[\rho]$  is the nucleus-electron attraction energy,

$$V_{ne}[\rho] = \int \rho(1) v(1) d\tau_1; \quad v(1) = -\sum_{\alpha} Z_{\alpha} (1/r_{\alpha 1}). \quad [4]$$

Of all densities satisfying [1], the one giving the lowest value of  $E[\rho]$  is the ground-state density; the corresponding value of  $\mu$  is the chemical potential of the ground state, equal to the negative of its electronegativity (2).

Exact implementation of [1] presently is impossible because the exact forms of  $T[\rho]$  and  $V_{ee}[\rho]$  are presently unknown. Both of these functionals may be regarded as composed of local and nonlocal components. In the present paper purely local components will be picked out, and the corresponding purely local density functional theory will be developed.

## LOCAL DENSITY FUNCTIONAL THEORY

By a local density functional is meant a functional whose functional derivative with respect to the density, at a point, is a function only of the density at that point (and not its derivatives or integrals). A local approximation for  $T[\rho]$  is an integral  $\int t(\rho) d\tau$ ; a local approximation for  $V_{ee}[\rho]$  is an integral  $\int v_{ee}(\rho) d\tau$ . That these are portions of kinetic and potential energies, respectively, in fact uniquely fixes the forms of  $t(\rho)$  and  $v_{ee}(\rho)$  (3); up to multiplicative constants they must be, respectively,  $\rho^{5/3}$  and  $\rho^{4/3}$ . The true whole functionals are universal functionals (1); universality therefore should be imposed on the local approximate theory. One is thus led to the local functionals

$$T_L[\rho] = \frac{3}{5} A(N) \int \rho^{5/3} d\tau, \quad V_{ee,L}[\rho] = \frac{3}{4} B(N) \int \rho^{4/3} d\tau, \quad [5]$$

where the quantities  $A(N)$  and  $B(N)$  may have some dependence on  $N$  but can have no dependence on  $v$ . The corresponding local energy functional is

$$E_L[\rho] = \frac{3}{5} A(N) \int \rho^{5/3} d\tau + \frac{3}{4} B(N) \int \rho^{4/3} d\tau + \int v \rho d\tau. \quad [6]$$

There is no alternative to this.

Completion of the theory requires determination of  $A(N)$  and  $B(N)$ . The simplest conceivable local functional description of a neutral atom would confer upon it a zero chemical potential. Another desirable result for a simple theory would be a  $Z^{7/3}$  dependence for neutral atom binding energies. Assuming both zero chemical potential for neutral atoms and a  $Z^{7/3}$  dependence of their energies gives the model that will be examined in this paper. In the next section it is shown that these assumptions in fact suffice to determine  $A(N)$  and  $B(N)$ ; namely,  $A(N) = A_0$  and  $B(N) = B_0 N^{2/3}$ , where  $A_0$  and  $B_0$  are constants. One consequently has, in place of [5] and [6],

$$T_L^0[\rho] = \frac{3}{5} A_0 \int \rho^{5/3} d\tau, \quad V_{ee}^0[\rho] = \frac{3}{4} B_0 N^{2/3} \int \rho^{4/3} d\tau, \quad [7]$$

and

$$E_L^0[\rho] = \frac{3}{5} A_0 \int \rho^{5/3} d\tau + \frac{3}{4} B_0 N^{2/3} \int \rho^{4/3} d\tau + \int v \rho d\tau. \quad [8]$$

There remains the values of  $A_0$  and  $B_0$ ; their values will turn out to be 6.4563 and 1.0058, respectively. With this energy functional, the stationary principle to be solved is

$$\delta(E_L^0[\rho] - \mu_L^0 N[\rho]) = 0, \quad [9]$$

where  $\mu_L^0$  is the chemical potential in the model.

## ATOMS

Rather than to start from [6] and prove [7], it is convenient first to carry through the whole analysis assuming [7] and then to demonstrate how [7] can be proved rather than assumed.

With the nuclear potential in the atom given by

$$v(1) = -Z/r_1, \quad [10]$$

the stationary principle [9] gives, suppressing the subscript 1,  

$$\mu_L^0 = A_0 \rho^{2/3} + B_0 N^{2/3} \rho^{1/3} - (Z/r) + (2/3)(1/N)V_{ee^0,L}[\rho]. \quad [11]$$

Introduce the parameter  $R$  by the formula

$$-(Z/R) = \mu_L^0 - (2/3)(1/N)V_{ee^0,L}[\rho]. \quad [12]$$

Then [11] becomes

$$A_0 \rho^{2/3} + B_0 N^{2/3} \rho^{1/3} + Z[(1/R) - (1/r)] = 0. \quad [13]$$

The value of  $R$  is determined by the normalization condition [2]. The density becomes zero continuously at  $r = R$ ; it could not be normalized if the atom did not have a finite radius. All of this follows from an analysis of the natural boundary conditions for the problem (4).\*

To obtain the final formula in the most compact form, let

$$s = r/R, \quad \rho(r) = (Z/A_0 R)^{3/2} [\chi(s)]^3, \quad [14]$$

and define

$$2\delta = (B_0 N^{2/3})(R/A_0 Z)^{1/2}. \quad [15]$$

Then one finds

$$\chi = -\delta + [\delta^2 - 1 + (1/s)]^{1/2}. \quad [16]$$

All atoms and ions are formally equivalent.

The energy components can be found by quadrature. The results may be compactly expressed in terms of the quantities

$$I_{k\ell}(\delta) = 8\pi \int_0^\infty \frac{x^k(\delta + x)dx}{(1 + 2\delta x + x^2)^{\ell+1}}, \quad [17]$$

of which the ones needed are

$$I_{00}(\delta) = 8\pi(1 - \delta^2)^{-1/2} \cos^{-1}\delta \equiv 8\pi J(\delta) \quad [18]$$

and

$$I_{33}(\delta) = [\pi/2(1 - \delta^2)^2] [-3\delta + (1 + 2\delta^2)J], \quad [19]$$

$$I_{53}(\delta) = [5\pi/6(1 - \delta^2)^2] [-\delta(5 - 2\delta^2) + 3J], \quad [20]$$

$$I_{43}(\delta) = [2\pi/3(1 - \delta^2)^2] [(2 + \delta^2) - 3\delta J], \quad [21]$$

$$I_{32}(\delta) = [3\pi/(1 - \delta^2)] [-\delta + J]. \quad [22]$$

In terms of these one finds

$$T_L^0[\rho] = (3/5)A_0^{-3/2}R^{1/2}Z^{5/2}I_{53}(\delta), \quad [23]$$

$$V_{ee^0,L}[\rho] = (3/4)B_0A_0^{-2}RZ^2I_{43}(\delta), \quad [24]$$

$$V_{ne^0}[\rho] = -A_0^{-3/2}R^{1/2}Z^{5/2}I_{32}(\delta), \quad [25]$$

and also

$$N = N[\rho] = A_0^{-3/2}R^{3/2}Z^{3/2}I_{33}(\delta). \quad [26]$$

Consequently

$$T_L^0[\rho] = \frac{Z^2 N^{1/3}}{A_0} \left\{ \frac{3I_{53}(\delta)}{5[I_{33}(\delta)]^{1/3}} \right\}, \quad [27]$$

$$V_{ee^0,L}[\rho] = \frac{ZN^{4/3}B_0}{A_0} \left\{ \frac{3I_{43}(\delta)}{4[I_{33}(\delta)]^{2/3}} \right\} \quad [28a]$$

$$= \frac{Z^2 N^{1/3}}{A_0} \left\{ \frac{3\delta I_{43}(\delta)}{2[I_{33}(\delta)]^{1/3}} \right\}, \quad [28b]$$

$$V_{ne^0}[\rho] = -\frac{Z^2 N^{1/3}}{A_0} \frac{I_{32}(\delta)}{[I_{33}(\delta)]^{1/3}}. \quad [29]$$

The relation that connects [28a] with [28b] is

$$B_0 = (Z/N) 2\delta [I_{33}(\delta)]^{1/3}. \quad [30]$$

The total energy is given by the formula

$$E_L^0[\rho] = -\frac{ZN^{1/3}}{A_0} \left\{ Z \frac{[I_{32}(\delta) - (3/5)I_{53}(\delta)]}{[I_{33}(\delta)]^{1/3}} - N \frac{[(3/4)I_{43}(\delta)B_0]}{[I_{33}(\delta)]^{2/3}} \right\}, \quad [31]$$

or by the formula

$$E_L^0[\rho] = -T_L^0[\rho] = -\frac{Z^2 N^{1/3}}{A_0} \left\{ \frac{3I_{53}(\delta)}{5[I_{33}(\delta)]^{1/3}} \right\}, \quad [32]$$

whereas the chemical potential is given by

$$\mu_L^0 = -\frac{Z^2 N^{-2/3}}{A_0} \left\{ \frac{I_{33}(\delta) - \delta I_{43}(\delta)}{[I_{33}(\delta)]^{1/3}} \right\} = \frac{7E_L^0[\rho] - 3V_{ne^0}[\rho]}{3N}. \quad [33]$$

Another quantity of interest is the ratio

$$r_F = -\frac{NV_{ne^0}[\rho]}{ZV_{ee^0,L}[\rho]} = \frac{2I_{32}(\delta)}{3\delta I_{43}(\delta)}. \quad [34]$$

All of these formulas are satisfied for any compatible values of the parameters  $A_0$ ,  $B_0$ ,  $\delta$ ,  $Z$  and  $N$ . Eq. 32 verifies that the virial theorem is satisfied; this arises from the identity

$$12I_{53}(\delta) + 15\delta I_{43}(\delta) - 10I_{32}(\delta) = 0. \quad [35]$$

The Hellmann-Feynman theorem also is satisfied; the right side of [34] follows from it or from [36].

The quantity  $B_0$ , and hence  $\delta$ , may be fixed by the one assumption: *The chemical potentials  $\mu_L^0$  for neutral atoms are zero.* Eqs. 32 and 33 show that this produces the identities

$$E_L^0 = -T_L^0 = (3/7)V_{ne^0} = -3V_{ee^0,L} \text{ (neutral atoms)}. \quad [36]$$

It also follows that  $\delta$  has the same value for all neutral atoms,  $\delta(N = Z)$ , the value of which is determined by solution of the equation

$$3(1 + 6\delta^2)J(\delta) = \delta(17 + 4\delta^2); \quad [37]$$

namely,

$$\delta(N = Z) = 0.53637838. \quad [38]$$

The corresponding value of  $B_0$  is, from [30],

$$B_0 = 1.00577635. \quad [39]$$

Note that neither [38] nor [39] depends on the value of  $A_0$ .

With [39] the value of  $B_0$ , [32] becomes

$$E_L^0[\rho] = -\frac{ZN^{1/3}}{A_0} [ZC_1(\delta) - NC_2(\delta)], \quad [40]$$

where

$$C_1(\delta) = \frac{I_{32}(\delta) - (3/5)I_{53}(\delta)}{[I_{33}(\delta)]^{1/3}}, \quad [41]$$

$$C_2(\delta) = \frac{0.5674920 I_{43}(\delta)}{[I_{33}(\delta)]^{2/3}}. \quad [42]$$

Also, [31] becomes

$$2\delta[I_{33}(\delta)]^{1/3} = 0.75433226(N/Z). \quad [43]$$

For each atom or ion, [43] determines  $\delta$ , which depends only on the ratio  $N/Z$ ; [40] then gives  $E_L^0$ . Together, these equations

\* This contrasts with Thomas-Fermi-Dirac theory, in which a different sign of the coefficient of  $\rho^{1/3}$  leads to a discontinuity at the boundary.

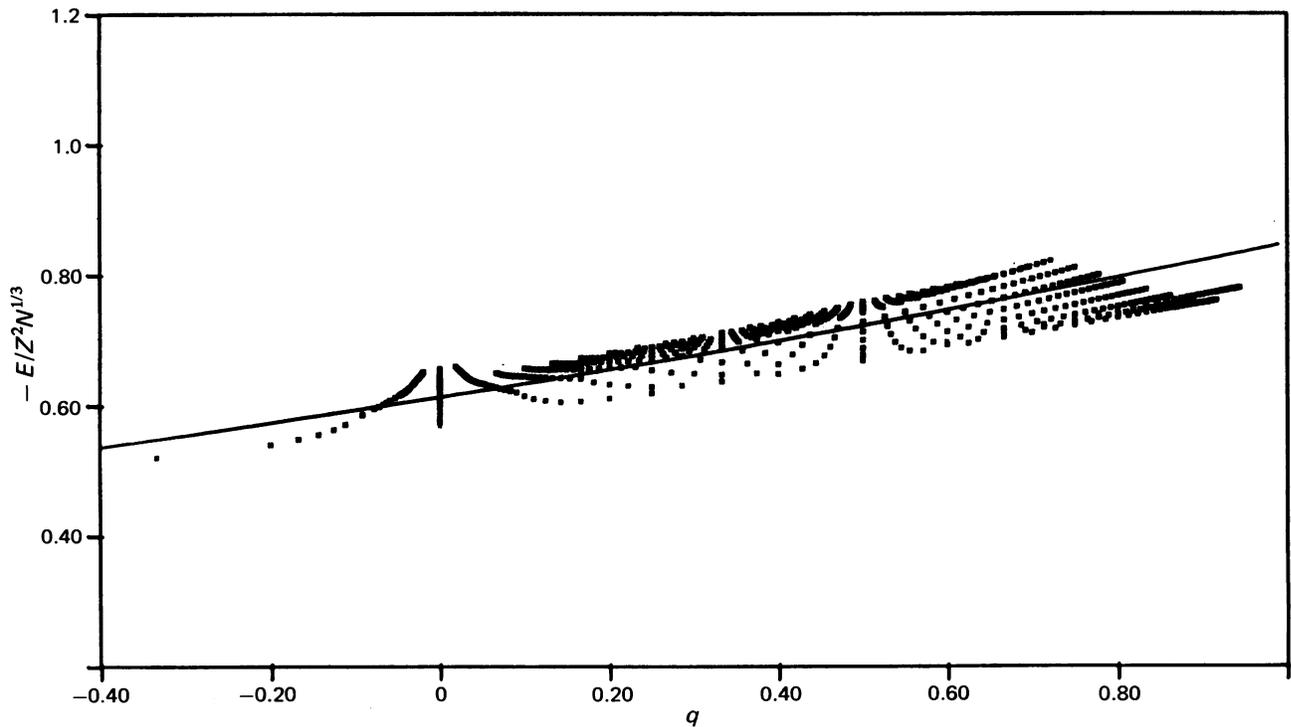


FIG. 1. Energies of atoms and ions as a function of fractional charge. Points are Hartree-Fock data (5). The curve is the theoretical prediction of [40].

determine the energy of all atoms and ions in terms of the single parameter  $A_0$ .

For a neutral species, [40] gives

$$E_L^0(N = Z) = -(3.9556/A_0)Z^{7/3}. \quad [44]$$

The Thomas-Fermi value of  $A_0$ , 4.7854, would give the numerical coefficient the value 0.8266, quite close to the corre-

sponding value in Thomas-Fermi theory, 0.7687. But for the present purposes a value chosen to give a good empirical fit of the whole periodic table appears preferable. That requires taking (see below)

$$A_0 = 6.4563, \quad [45]$$

which gives

$$E_L^0(N = Z) = -0.6127 Z^{7/3}. \quad [46]$$

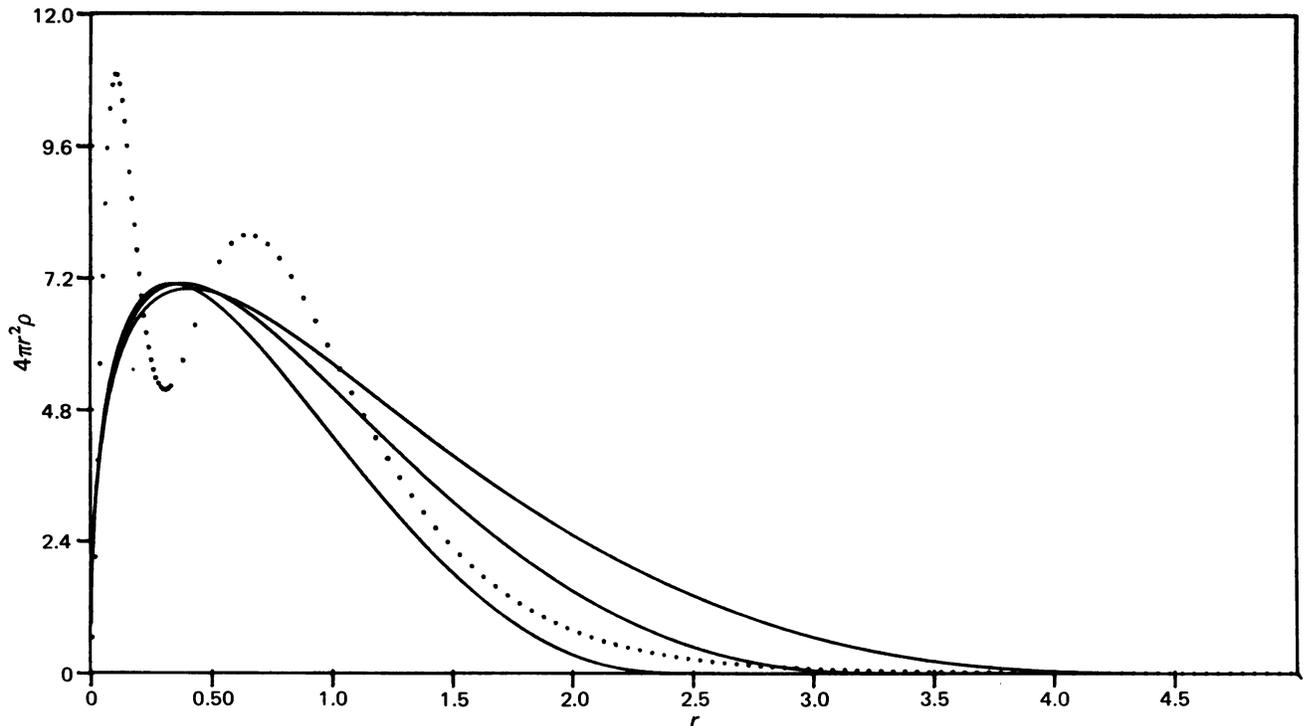


FIG. 2. Radial distribution functions for  $\text{Ne}^{+2}$ ,  $\text{Ne}$ , and  $\text{Ne}^{-2}$ . The broken curve is the Hartree-Fock radial distribution function for  $\text{Ne}$  (5).

Table 1. Various functions of the fractional charge  $q$

$q$	$\delta$	$-\frac{1}{A_0} C_1$	$\frac{1}{A_0} C_2$	$r_F$
-0.4	0.9008	0.7879	0.1800	7.3531
-0.2	0.7027	0.8035	0.1920	7.1689
0.0	0.5364	0.8169	0.2042	7.0000
0.2	0.3952	0.8281	0.2166	6.8446
0.4	0.2744	0.8369	0.2292	6.7012
0.6	0.1701	0.8433	0.2420	6.5685
0.8	0.0794	0.8471	0.2549	6.4455

See text for definitions of quantities tabulated.

Consider now the question whether [7] could have been derived as a consequence of some other postulate. The answer is yes, if one assumes [46] itself and unknown  $A(N)$  and  $B(N)$ , one finds on working the whole theory through that  $dA(N)/dN = 0$  and  $dB(N)/dN = (2/3)(B/N)$ , which give just [7].

**CALCULATIONS ON ATOMS**

By [43], all quantities which are functions of  $\delta$  are functions of  $N/Z$ . Or, they may be taken to be functions of the fractional deviation from neutrality, the parameter  $q = (Z - N)/Z$ . Table 1 gives some typical values.

Fig. 1 shows how well the theoretical formula [40] predicts energies of atoms and ions.<sup>†</sup> With the data base taken to be the entire set of energies from an available table of Hartree-Fock calculations (9), the theoretical curve for the quantity  $E/Z^2N^{1/3}$  as a function of  $q$ , shown in Fig. 1,<sup>‡</sup> has a root-mean-square error of 0.0334, or typically about 5%, whereas the best least-squares linear fit of the same data, given by the formula

$$-E(N,Z)/Z^2N^{1/3} = 0.6343 + 0.1721q, \quad [47]$$

has a root-mean-square error of 0.0270, just a little less. The value of  $A_0$  for the theoretical curve was chosen to make unity the average over the whole data set of the ratio of computed to Hartree-Fock energy. Actual Hartree-Fock energy components do not confirm the prediction of a constant  $r_F$  value for a given value of  $q$ , but they do confirm the prediction from Table 1 that a decrease in  $N$  for a given  $Z$  should decrease the  $r_F$  value. Negative ions exist in this model, for all values of  $q$  greater than  $-0.5$ . However, electron affinities of neutral atoms are negative.

Fig. 2 shows the radial distribution functions for the species  $Ne^{+2}$ ,  $Ne$ , and  $Ne^{-2}$ , as determined from [13]-[16]. Also shown on the figure is the Hartree-Fock distribution function for  $Ne$ . The comparison is favorable, but it is less so for atoms of higher  $Z$ . As  $Z$  increases, the whole local density functional density shrinks as  $Z^{-1/3}$ , whereas real densities retain more slowly dying-off tails.

**MOLECULES**

The molecular problem is formally the same as the atomic problem, the only difference being that the nuclear potential is given by [4] instead of by [10]. This potential is itself the variable in terms of which the density can be expressed. One obtains for any molecule, for any nuclear configuration, the result that it has a finite size, with its electron density extending

<sup>†</sup> For previous discussions of this problem, see the works of Fraga (5, 6), Goodisman (7), and March and White (8).

<sup>‡</sup> This way of representing and fitting the data emphasizes percentage rather than absolute errors in energies. The analogue of [47] for a fit of  $E$  itself is  $-E = Z^2N^{1/3}(0.6510 + 0.1800q)$ , with a root-mean-square error of 35.

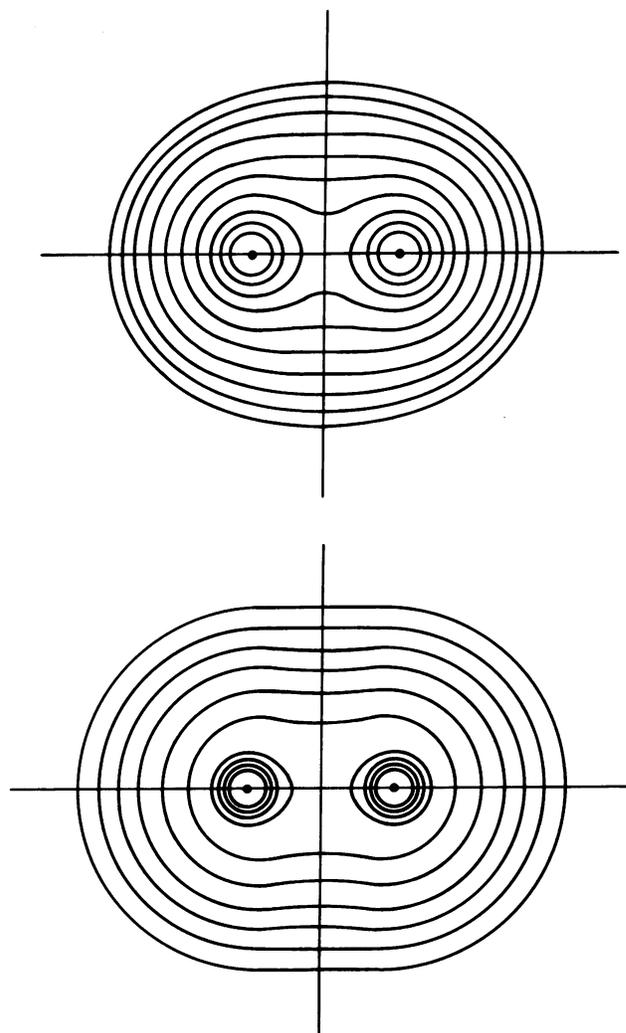


FIG. 3. Contours of electron density for  $B_2$ . (Upper) Local density functional theory, with  $V_{max} = 2$ . (Lower) Molecular orbital theory [after Wahl (ref. 10)]. Adjacent contours differ by factors of 2 in each case.

from the nuclei out to the surface (or surfaces) at which the nuclear potential has the maximum value  $v_{max}$ , at which the density becomes zero continuously. In terms of the variable

$$s_M(1) = \frac{v_{max}}{v(1)}, \quad [48]$$

and the parameter

$$2\delta_M = (B_0N)^{2/3}(A_0v_{max})^{-1/2}, \quad [49]$$

one finds, in complete analogy with [16],

$$\chi_M = -\delta_M + [\delta_M^2 - 1 + (1/s_M)]^{1/2}, \quad [50]$$

where, in analogy with [14],

$$\rho[v(1)] = (-v_{max}/A_0)^{3/2}[\chi_M(s_M)]^3. \quad [51]$$

Completion of the analysis for any molecule requires carrying through the quadratures implied in [6]. That aside, the general result is already evident from [50]: *In local density functional theory, contours of the bare-nuclear potential are contours of the total electron density.* That this is an approximate characteristic of real molecules is evident from Fig. 3,

in which are displayed contour diagrams for the molecule  $B_2$ .

### DISCUSSION

The appeal of local density functional theory is three-fold. It is simple and easy to implement. It gives interesting predictions of energies and electron densities, for both charged and uncharged species. Most important, it provides an attractive starting point for systematic development of accurate density functional theory.

It was Fraga who long ago (5) first demonstrated that the ratio of [34] was surprisingly constant for neutral atoms, and recent work by Politzer (11), Ruedenberg (12), and others has revealed that such constancies persist for molecules. The present analysis provides a physical basis for regularities of this kind, and extends them to charged species.

The implied assumption of local density functional theory is that the approximation

$$V_{ee}[\rho] \approx V_{ee}^0, L[\rho] = 0.75N^{2/3} \int \rho^{4/3} d\tau \quad [52]$$

will give not unreasonable values of  $V_{ee}$  for actual systems. This can be checked by comparing actual  $V_{ee}$  values for Hartree-Fock wavefunctions for atoms with values computed from [52] by using Hartree-Fock densities (9). For the atoms He through Co, the ratio of actual to computed  $V_{ee}$  values varies from 0.72 to 1.07; from F through Co this ratio ranges only from 1.00 to 1.07. Another comparison is with the value of the self-repulsion energy  $(1/2) \iint \rho(1)\rho(2)(1/r_{12})d\tau_1d\tau_2$  for a uniform distribution of charge in a sphere of radius  $R$ . The correct value is  $0.6N^2/R$ , whereas [52] gives  $0.5N^2/R$ .

Charge densities obtained from theories employing [52] nevertheless are deficient in comparison with actual densities; they fall to zero too fast, especially for high  $Z$ . This is a firm prediction from local density functional theory. It should prove an advantage when one proceeds to develop the nonlocal contributions to the theory by gradient expansion methods, because the finite boundaries of the local approximation permit inclusion of higher-order gradient corrections than otherwise would be possible.

To assume chemical potentials of neutral atoms to be zero denies an essential characteristic of actual atoms, but nevertheless it is natural in the simplest local theory.

It will be interesting to study incorporation of [52] into various other models. One could use [52] together with a correct wave-mechanical  $T[\psi]$ , for instance, or in a density functional model including Weizsacker corrections to  $T[\rho]$ . One may also wish to consider more elaborate (nonlocal) self-consistent prescriptions for determining the coefficient of the integral  $\int \rho^{4/3} d\tau$ . Without going that far, it certainly will be worthwhile to study the result of dropping the assumption [46], which will permit a more general form for  $B(N)$ , in particular the enticing form

$$B(N) = B_0N^{2/3} + B_1, \quad [53]$$

where  $B_0$  and  $B_1$  are constants.

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