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A simple approach for the direct calculation of electron density bypassing the Schrödinger equation

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Abstract

In this paper, we review two of our recent works dealing with a quadratic equation for the direct calculation of the electronic density and properties of atoms and ions. The equation incorporates a first-gradient kinetic energy correction, Dirac exchange and Wigner-type correlation contributions. Its results for various atomic and ionic systems are surprisingly good, considering the simplicity of the equation. The equation also yields a universal density criterion which unifies and correlates various empirical radii (covalent, ionic, Van der Waals and Wigner–Seitz radii) as well as other properties of atoms and ions.

Key words: Electron density, properties of atoms and ions, quadratic equation.

1. Introduction

There was this dreamy, old Russian prospector in search of the largest diamond in the world. According to his own information and calculation, the diamond was 2 km long, 1 km wide and 1/2 km deep. It was believed to have been formed by the impact of a meteorite on a remote and inaccessible Siberian coalfield. The old man spent his whole life hunting for the diamond but never found it. He just kept on getting slightly larger and larger pebbles of diamond which always beckoned him tantalizingly towards the large mythical diamond. He was only interested in the pleasure of seeing this diamond before anybody else did but he died without ever catching a glimpse of it.

For more than two decades, we too have been pursuing a dream—the dream of obtaining a *single* equation for the *direct* and accurate calculation of electron density in atoms, molecules and solids, bypassing the many-electron wave function and the Schrödinger equation. In this lecture, based on two of our recent papers[1,2], we describe a simple approach for the direct, approximate calculation of the electronic

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describe a simple approach for the direct, approximate calculation of the electronic density and properties of atoms and ions in their ground states. Some interesting consequences of this approach are also described (for various concepts and formalisms associated with the electron density as well as its significance in chemistry, the reader may consult Deb *et al*[3–9]).

2. The approach

In order to derive a single equation for the direct calculation of electron density in many-electron systems, we proceed according to the following steps:

(i) Write the electronic energy $E[\rho]$ as a functional of the three-dimensional electron density $\rho(\vec{r})$ (a functional may be regarded as a function of a function and is defined as an integral[10]).

(ii) Minimize $E[\rho]$ with respect to all trial densities (variation principle), preserving the total number(N) of electrons such that

$$\int \rho(\vec{r})d\vec{r} = N \tag{1}$$

(iii) This procedure yields the Euler–Lagrange equation for directly determining the density $\rho(\vec{r})$, *viz.*,

$$\frac{\delta E\,[\rho]}{\delta \rho} = \mu \tag{2}$$

where μ is a Lagrange multiplier (constant) and is called the chemical potential because it is the zero-temperature limit of the chemical potential defined for the finite-temperature grand canonical ensemble[11].

(iv) The terms in the energy functional $E[\rho]$ are as follows:

$$E[\rho] = \text{kinetic energy} + \text{electron–nuclear attraction energy} + \text{interelectronic Coulomb repulsion energy} + \text{exchange energy} + \text{correlation energy} \tag{3}$$

Of these, the kinetic, exchange and correlation energy functionals for an atom, molecule or solid are unknown. This is a very serious problem and might even be unsolvable. In addition, there are other problems as we will see later.

Clearly, we need to use approximate functionals for three unknown functionals. A great deal of work has been done in searching for better approximations to the kinetic[12], exchange[13–15] and correlation[13–15] functionals.

2.1. *Choosing the kinetic energy functional,* $T[\rho]$

We write $T[\rho]$ as

$$T[\rho] = \int t[\rho]d\vec{r} \tag{4}$$

where $t[\rho]$ is the corresponding (interacting) kinetic energy density. The required properties of $T[\rho]$ and $t[\rho]$ are: (i) global accuracy, (ii) local accuracy, and (iii) proper functional derivatives, $\delta T/\delta\rho$ and $\delta t/\delta\rho$.

Over the years, there have been many proposals for $T[\rho]$ and $t[\rho]$, none truly satisfactory. In particular, the fact that $t[\rho] \to \infty$ as $r \to 0$, for atoms, seems to have been ignored.

As an approximation for atomic systems, we replace $T[\rho]$ by $T_S[\rho]$, the noninteracting kinetic-energy functional, such that

$$T[\rho] = T_S[\rho] + \text{a positive term.} \tag{5}$$

We then choose $T_S[\rho]$ as a combination of the Thomas–Fermi term and a first-gradient correction, *viz.*, (atomic units employed throughout this paper, unless otherwise specified)

$$T_S[\rho] = C_k \int \rho^{5/3}(\vec{r})\, d\vec{r} - \frac{1}{40} \int \frac{\vec{r}.\nabla\rho}{r^2}\, d\vec{r} \tag{6}$$

$$C_k = (3/10)\,(3\pi^2)^{2/3}. \tag{7}$$

The factor 1/40 may be traced to the fact that

$$\frac{1}{5} T_w > -\frac{1}{40} \int \frac{\vec{r}.\nabla\rho}{r^2}\, d\vec{r} \tag{8}$$

where T_w the Weizsäcker correction is given by

$$T_w = \frac{1}{8} \int \frac{(\nabla\rho)^2}{\rho}\, d\vec{r}. \tag{9}$$

The term, $(\vec{r}.\nabla\rho)/r^2$ is a component of the term $(-1/4\ \nabla^2\rho)$ which occurs in the kinetic energy density of atomic systems. With this prescription, it is clear that $t_s[\rho]$, as given in eqn (6), goes to infinity as $r \to 0$; it has excellent local accuracy[16] over the range $0 \leq r \leq \infty$. $T_s[\rho]$ has high global accuracy and, using Hartree–Fock spherical atomic densities[17], gives kinetic energies to within 0.4% error, the error being always negative[16], in view of eqn (5). It also satisfies the correct scaling properties[18]. For numerical *self-consistent* calculations, the parameter (1/40) will be replaced by (1/32).

2.2. *Choosing the exchange energy functional* $E_x[\rho]$

In order to keep the approach as simple as possible, we choose the Dirac exchange functional

$$E_x[\rho] = -C_x \int \rho^{4/3}(\vec{r})d\vec{r};\ C_x = (3/4\pi)\,(3\pi^2)^{1/3}. \tag{10}$$

Like the kinetic energy functional, a first-gradient correction can be incorporated in eqn (10), but we refrain from doing so for reasons which will be clear below. It may be noted that the Dirac exchange is less in magnitude than the Hartree–Fock exchange energy.

2.3. *Choosing the correlation energy functional* $E_c[\rho]$

This is a rather difficult problem. It has not been satisfactorily tackled so far although many forms have been suggested. Here, we adopt Wigner's expression for $E_c[\rho]$ which has been parametrized by Brual and Rothstein[19].

$$E_c[\rho] = -\int \frac{\rho(\vec{r})}{9.810+21.437\ \rho^{-1/3}(\vec{r})}\, d\vec{r}. \tag{11}$$

Correlation energy values calculated for atomic systems, by using eqn[11], are generally *overestimated* by a few per cent[1]. Therefore, the above $E_x[\rho]+E_c[\rho]$ is likely to be a good approximation to the ground–state exchange–correlation energy due to a partial cancellation of errors. It may also be noted that both $E_x[\rho]$ and $E_c[\rho]$ are local functionals of the electron density.

The electron–nuclear attraction energy and the interelectronic coulomb repulsion energy functionals can readily be written as

$$V_{en}[\rho] = -\int (Z/r)\rho(\vec{r})d\vec{r}; \tag{12}$$

and

$$V_{coul}[\rho] = \frac{1}{2}\iint \frac{\rho(\vec{r})\ \rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}d\vec{r}\,'. \tag{13}$$

where Z is the nuclear charge of the atomic system.

With all the component functionals written above, the total energy functional now becomes

$$\begin{aligned} E[\rho] = {} & (3/10)\ (3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r} - (1/32)\int \frac{\vec{r}.\nabla\rho}{r^2}\, d\vec{r} \\ & -\int (Z/r)\rho(\vec{r})\ d\vec{r} + (1/2)\iint \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\ d\vec{r}\,'. \\ & - (3/4)\ (3\pi^2)^{1/3}\int \rho^{4/3}(\vec{r})d\vec{r} - \int \frac{\rho(\vec{r})}{9.810+21.437\ \rho^{-1/3}\ (\vec{r})}\, d\vec{r}. \end{aligned} \tag{14}$$

In eqn (14), the second term on the right hand side has the factor (1/40) replaced by (1/32). The former is preferred for Hartree–Fock densities while the latter is preferred for densities calculated *self-consistently* according to eqn (14); as we will see later, such self-consistent densities are not of Hartree–Fock quality.

Using eqn (14), the Euler–Lagrange equation (2) now becomes a *quadratic* equation

$$A\theta^2 + B\theta + C = 0 \tag{15}$$

where

$$\theta = \rho^{1/3} \tag{16}$$

$$A = -5/3\ C_k = -(1/2)\ (3\pi^2)^{2/3} \tag{17}$$

$$B = 4/3\ C_x = (1/\pi)\ (3\pi^2)^{1/3} \tag{18}$$

$$C = \mu + U(r) - (1/32)\ (1/r^2) + \frac{9.81 + 28.583\bar{\rho}^{1/3}}{(9.81 + 21.437\bar{\rho}^{1/3})^2}. \tag{19}$$

$$U(r) = \text{Electrostatic potential at } r = (Z/r) - \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,'. \tag{20}$$

The quadratic equation (15) is rather surprising and disquieting, because quantum mechanical equations are known to be either differential or integral or integro-differential, for calculations on many-electron systems. Indeed, eqn (15) appears to be rather naive and one's first impulse might be to discard it. But, before discarding the equation, it is necessary to examine it carefully.

Equation (15) can be solved numerically and point-to-point in a self-consistent manner[1] starting with a trial ρ and a trial μ, subject to the normalization constraint. The solution yields self-consistent ρ and μ. Only the positive solution of the quadratic equation is taken, *i.e.*, $\theta = \rho^{1/3}$ is positive. It may be noted that θ is an unusual 'orbital' in the sense that its cube, not the square, gives the electron density.

2.4. *Tests for internal consistency of the quadratic equation*

Since the wave function is being bypassed in our calculations, we must ensure that the calculated $\rho(\vec{r})$ satisfies the following conditions which would ensure that our methodology is internally consistent:

(i) N-representability

$$\int \rho(\vec{r})\, d\vec{r} = N;\ \rho(\vec{r}) \geq 0,\ \forall \vec{r}. \tag{21}$$

This ensures that our calculated electron density corresponds to an antisymmetric wave function.

(ii) Cusp condition

$$\left(\frac{\delta\rho}{\delta r}\right)_{r=0} = -2Z\rho(0) \tag{22}$$

where Z is the nuclear charge. This ensures that the density falls off from the nuclear site at the correct rate.

(iii) Asymptotic condition

$$\rho(r) \sim \exp\left[-2(-2\mu)^{1/2}\, r\right],\ r \to \infty.$$

This is trivially satisfied while conditions (i) and (ii) are built into our calculation.

(iv) The virial theorem

Although $2T[\rho] + V[\rho] = 0$, (23)

where $T[\rho]$ is the interacting kinetic energy and $V[\rho]$ is the total potential energy,

$$2T_s[\rho]+V[\rho] \neq 0. \tag{24}$$

In fact, it can be shown[1] that the correct statement of virial theorem in the present context is

$$-V/T_s > 2. \tag{25}$$

Condition (25) is generally, although not invariably, satisfied in our calculations. However, $2T_s[\rho] + V[\rho]$ is always close to zero in our calculations.

(v) The chemical potential $\mu = (\delta E/\delta N)$ should satisfy the following conditions:

(a) μ is negative for a neutral atom A and its cation.
(b) μ is positive for the anion of A.
(c) $|\mu(A^+)| > |\mu(A)|$. (26)

(vi) The electrostatic potential $U(r)$ for a mononegative ion (A^-) should satisfy the following conditions[20]:

(a) $U(r)$ passes through a minimum at a finite, non-zero r, say r_m.
(b) r_m satisfies the relations

$$Z = 4\pi \int_0^{r_m} r^2 \rho(r)\, dr \tag{27}$$

and

$$U(r_m) = -4\pi \int_{r_m}^{\infty} r\rho(r)\, dr \tag{28}$$

where Z is the nuclear charge of the anion. Conditions (v) and (vi) above are satisfied in our calculations. It may be noted that mononegative ions constitute a challenge for any quantum-chemical method because of the diffuseness of the (extra) electron cloud.

2.5. Results and discussion

Our computer program, based on the above method, operates on an Apollo-3000 workstation in our laboratory. The program has been executed on mainframe computers as well. It can be applied to any atom or ion, including undiscovered systems; the only necessary inputs are Z and N for a given system.

Using the calculated electron density, several average values (moments) can be calculated by using the definition

$$\langle f \rangle = \int \rho(\vec{r}) f \, d\vec{r} \tag{29}$$

where $f = r, r^2, 1/r, 1/r^2$ in the present calculations. While $\langle r \rangle$ and $\langle r^2 \rangle$ probe the long-range accuracy of the calculated density, $\langle 1/r \rangle$ and $\langle 1/r^2 \rangle$ probe its short-range accuracy. It is well-known that $\langle r \rangle$ is associated with dipole moment, $\langle r^2 \rangle$ with diamagnetic susceptibility, $\langle 1/r \rangle$ with potential energy, nuclear magnetic shielding, $\langle 1/r^2 \rangle$ with electric field, force and so on.

Since the present method is essentially a Thomas–Fermi–Dirac-type method, the plot of radial density ($4\pi r^2 \rho$) against $r^{1/2}$ for any atom or ion shows only *one* peak, indicating the absence of shell structure in these calculations. This is characteristic of Thomas–Fermi–Dirac-type methods. Table I reports the calculated results on several neutral and ionic systems. For other systems and a detailed discussion we refer to Deb and Chattaraj[1]. However, one can make the following observations from Table I:

(a) Comparison with Hartree–Fock calculations[17,21] shows satisfactory agreement with our results. Since our calculations include correlation energy, in every case our total energy has gone below the Hartree–Fock energy.

(b) The internal consistency tests mentioned in Section 2.5 can be verified from Table I (except the $U(r)$ test).

(c) The method concentrates more electron density than necessary near the nucleus. This is also a feature of Thomas–Fermi–Dirac-type calculations. Thus, the larger $\langle 1/r \rangle$ and $\langle 1/r^2 \rangle$values in our calculations are generally accompanied by smaller $\langle r \rangle$ and $\langle r^2 \rangle$ values (see Deb and Chattaraj[1] for additional explanation).

(d) It is very difficult to calculate the electron affinity of alkaline earth metal atoms. Comparison with relativistic density–functional calculations[22] for Ca and Ba shows our results to be satisfactory.

(e) Figure 1 shows that Ca^- shows an electrostatic potential minimum at $r_m = 3.648$ au. The calculated Z from eqn (27) is 20.02 (the actual value is 20) and $U(r_m)$ from eqn (28) is -0.2038 compared with the actual value of -0.1995 au.

For other aspects and features of these calculations, we refer to Deb and Chattaraj[1].

To conclude this section, we make the following observations:

(a) The quadratic equation (15) is viable, internally consistent and capable of rapidly delivering good quality results for atoms and ions, especially for negative ions. However, the method is not applicable to H^- ion.

(b) A *single* 'orbital' is defined for the whole system. This is $\rho^{1/3}$ and not $\rho^{1/2}$ as in the usual orbital approach.

(c) The computational effort is minimal and does not increase significantly with the number of electrons in the system.

Table I

Electronic properties (au) of three neutral atoms as well as their cations and anions in their ground states

Electronic properties	*Systems*								
	At^+	At	At^-	Ca^+	Ca	Ca^-	Ra^+	Ra	Ra^-
T_s	21371.0 (21266.517)	21371.1 (21266.809)	21370.0 (21266.924)	697.65 (676.569)	698.19 (676.756)	699.68	23175.2 (23094 042)	23175.1 (23094.214)	23169.9
$-V$	42760.2 (42533.048)	42760.5 (42533.674)	42759.3 (42533.862)	1385.6 (1353.139)	1386 3 (1353.514)	1387.7	46423.5 (46188 188)	46423.7 (46188.504)	46418.4
$-E$	21389.2 (21266 531)	21389.4 (21266.865)	21389.4 (21266.958)	688.0 (676 570)	688.1 (676.758)	688.1	23248.3 (23094 146)	23248.5 (23094.290)	23248.5
$-V/T_s$	2.001 (2.000)	2.001 (2.000)	2.001 (2 000)	1.986 (2.000)	1.986 (2.000)	1 983	2.003 (2.000)	2.003 (2.000)	2.003
μ	−0 51	−0.16	0.12	−0.41	−0.07	0 10	−0.51	−0.16	0.12
IP	—	0.2 (0.334)	—	—	0.1 (0.188)	—	—	0.2 (0.144)	—
EA	—	0.0 (−0 0927)	—	—	0.0 (−0 0048)	—	—	0.0 (−0 0047)	—
$\langle r \rangle$	50.34 (49.624)	53.74 (53.062)	59.32 (57.107)	14.57	17.88	22.06	51.74 (54.015)	55.14 (60.221)	60.59
$\langle r^2 \rangle$	73.23 (68.534)	85.48 (81.565)	114.3 (99.862)	21.17	32.92	53.58	75.15 (90 122)	87.40 (132.828)	115 0
$\langle 1/r \rangle$	596.0 (594.597)	596.2 (594 920)	596.3 (595.195)	81 94	82 28	82 68	624.9 (622.884)	625 2 (623.067)	625.2
$\langle 1/r^2 \rangle$	48312 (38088.971)	48312 (38088.800)	48312 (38088 736)	2452.7	2453.0	2454 1	51985 (40938.032)	51985 (40938.232)	51979

T_S=Noninteracting kinetic energy, V=Potential energy, E=Total energy, μ=Chemical potential, IP=E (cation)–E(neutral), EA=E (anion)–E(neutral). Values [17,21,22] in parentheses are for comparison. All results are taken from Deb and Chattaraj[1].

(d) Internal details such as atomic shell structure are missing in these calculations, but the equation should be satisfactory in cases where such details are not required.

(e) A quadratic equation may be envisaged for molecules and solids. If successful, this would be revolutionary.

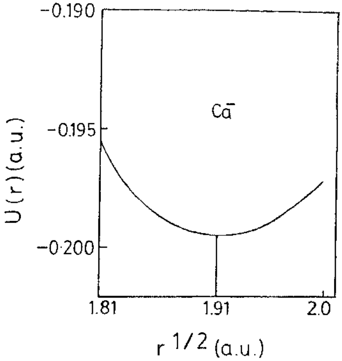


FIG. 1. Electrostatic potential, eqn (20), for the Ca$^-$ ion, plotted against $r^{1/2}$, in atomic units. The minimum occurs at $r^{1/2}$ = 1.91 au. (reproduced from Deb and Chattaraj[1] by permission.)

3. A universal density criterion for correlating various empirical radii in molecules, solids and solutions

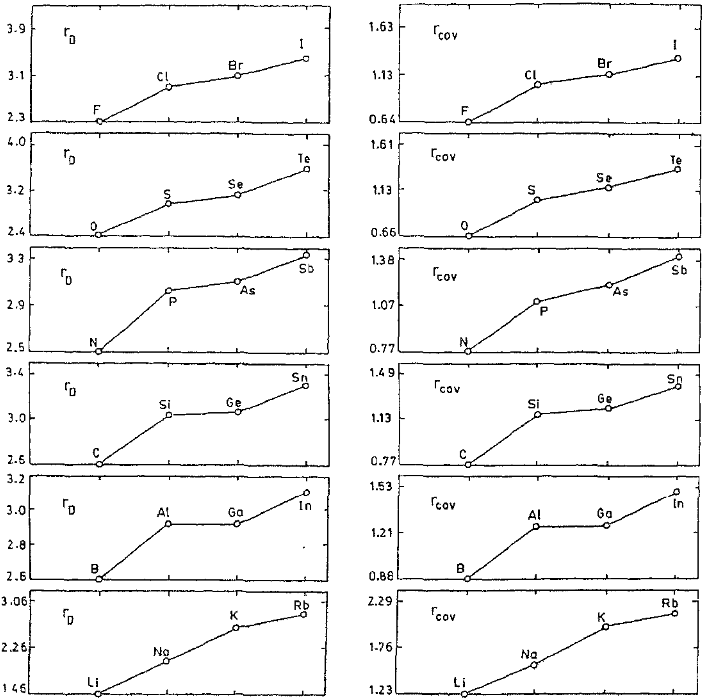
In structural chemistry, *empirical* concepts and values of covalent radii(r_{cov}), ionic radii (r_{ion}), Van der Waals radii(r_{vdw}), Wigner–Seitz radii (r_{ws}) for molecules, solids and solutions have proved to be very useful. These radii are transferable from one environment to another within a small range of variations. In this section we discuss a proposition[2] that in any environment an atom or ion 'looks for' that distance at which it acquires a universal density value. In case this proposition is correct, one should be able to correlate this distance with any empirical radius and perhaps with other electronic properties as well.

Consider again, eqns (15)–(20). Let us choose an r-value, designated as r_D, so that C in eqn (19) vanishes at r_D. Therefore, from eqn (15), the density $\rho_D = \rho(r_D)$ is given by

$$\rho_D = -(B/A)^3 = (4C_x/5C_k)^3 = 0.008714 \tag{30}$$

which is a *universal* value. Accordingly, this r_D is defined[2] as the *characteristic,* finite, non-zero value of r at which an atom or ion acquires the universal density value of 0.008714. This r_D may be used to correlate and unify the various empirical radii.

Since the quadratic equation[15] itself does not show shell structure, we have computed r_D for about 100 atoms and ions by using their Hartree–Fock densities[17,21] Detailed results and their discussion have been presented in Deb *et al*[2]. Here we discuss only some of the salient features of our results.

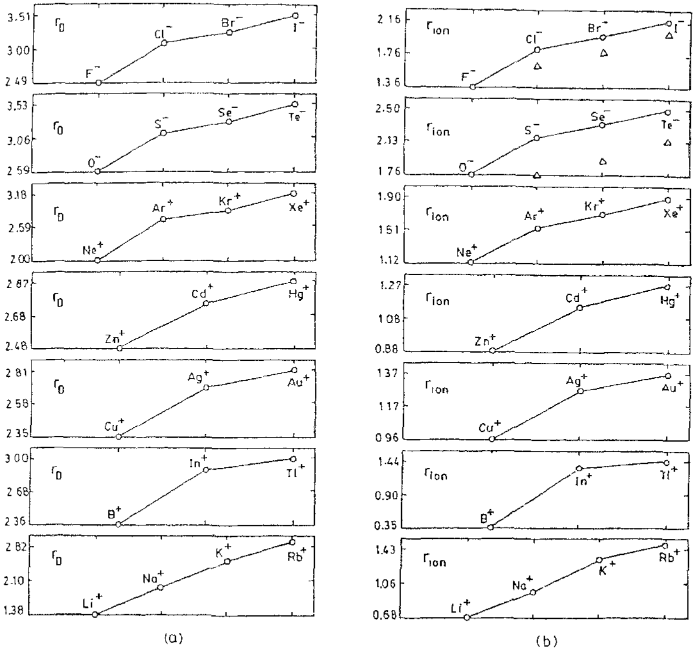


(a) (b)

FIG 2. Variations in (a) r_D (au) and (b) r_{cov} (Å) among vertical groups of atoms (reproduced from Deb *et al*[2] by permission).

Figures 2–5 depict the variations in r_D corresponding to the variations in r_{cov}, r_{ion}, r_{vdw} and r_{ws}, respectively, among vertical groups of atoms. There are striking similarities between the variations in r_D and those in the different types of empirical radii. Apart from these empirical radii, r_D also correlates linearly with the first ionization potential, electronegativity, softness[11], logarithm of dipole polarizability and of London dispersion coefficient(C_6), etc. for groups of atoms[2].

However, the horizontal variations in r_D and r_{cov} are *not* identical, because r_D has more information content than any type of empirical radius. Figure 6 depicts such



(a) (b)

FIG. 3. Variations in (a) r_D (au) and (b) r_{ion} (Å) among vertical groups of monopositive and mononegative ions (reproduced from Deb *et al*[2] by permission).

variations for the K-period, Rb-period and the lanthanons. The variations in r_D appear more interesting than those in r_{cov}. Especially interesting are the Nessie (the legendary Loch Ness Monster)-type variations in r_D for the K- and Rb-periods. In contrast to the r_{cov} variations, the r_D variations pinpoint important characteristics in the electronic configuration. In particular, half-filled and completely filled subshells are clearly picked out. Among the lanthanons, the lanthanide contraction is clearly discernible in r_D but not in r_{cov}. Obviously r_{cov} does not clearly show such important characteristics of the electronic configuration.

The percentage of the total electronic charge within a sphere of radius r_D is given by

$$N_D = \frac{100\, q_D}{N} \tag{31}$$

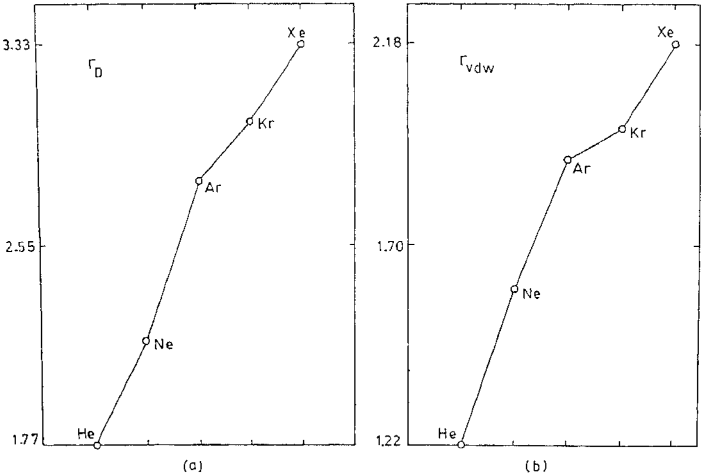


FIG. 4. Variations in (a) r_D (au) and (b) r_{vdw} (Å) among the noble gas atoms (reproduced from Deb *et al*.[2] by permission).

where
$$q_D = \int_0^{r_D} \rho(\vec{r})\, d\vec{r}. \tag{32}$$

For the nearly one hundred atoms and ions examined by us, N_D exceeds 95% on the average and exceeds 98% for a number of systems.

To conclude this section, we make the following observations:

(a) The characteristic radius r_D is a quantity of great interest and contains much more information than any of r_{cov}, r_{ion}, r_{vdw}, r_{ws}.

(b) Since r_D is linearly related to a host of electronic properties of atoms and ions, it is clear that all these properties are interrelated by a *single, master equation*. The search for such a *non-empirical* equation should be rewarding.

(c) A fundamental question arises concerning the universality of our results: Why should r_D and the universal density value of 0.008714, obtained from the ratio of the Dirac exchange constant to the Thomas–Fermi kinetic energy constant, be of such crucial importance?

(d) Although an answer to this question is not available at present, through r_D we have tried to provide a unifying, universal explanation for the existence of various empirical atomic and ionic radii.

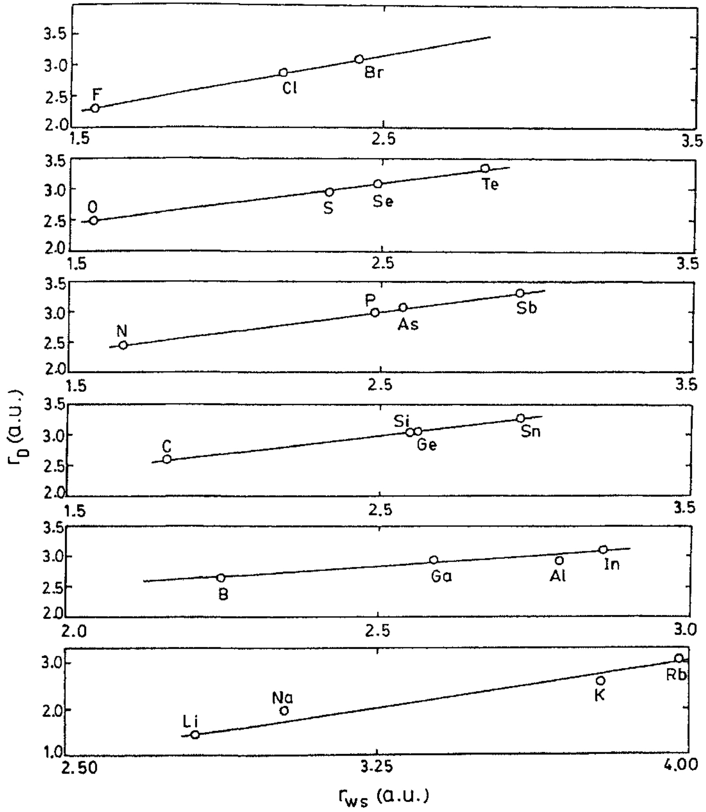


FIG. 5 Plot of r_D (au) against r_{ws} (au) for vertical groups of atoms (reproduced from Deb *et al*[2] by permission).

4. Conclusions

The formalism and results presented in this paper strongly suggest that it is necessary to examine algebraic equations, for the direct calculation of electron density in many-

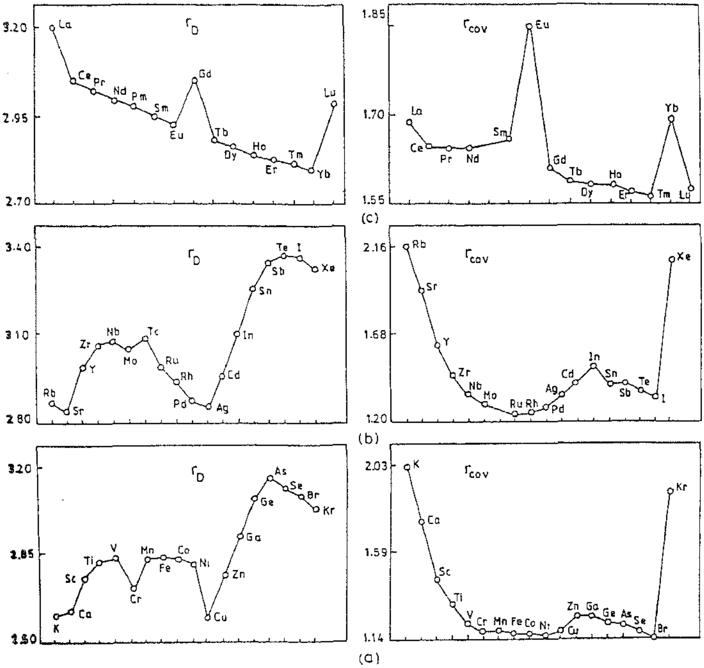


FIG 6 Horizontal variations in r_D (au) and r_{cov} (Å) among (a) third row atoms, (b) fourth row atoms, and (c) lanthanons (reproduced from Deb *et al*[3] by permission).

electron systems. Such equations, by virtue of their simplicity, may reveal interesting, unifying features which may otherwise remain concealed from us. The extension of such algebraic equations to excited states and time-dependent situations should be of considerable interest.

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