Asian Journal of Chemistry Vol. 10, No. 4 (1998), 844–847

Classical Coulomb Energies $J_L(\rho)$ and $J_{NL}(\rho)$ of an Atomic Charge Distribution Studies with Partitioned Charge Density Function

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Density functional (DF) theory provides a methodology to study atomic and molecular systems in terms of the electron density function $\{\rho(r)\}$ instead of the many-particle wave function $\psi(r)$. The Pacios density function has been used to calculate the $J_L(\rho)$ and $J_{NL}(\rho)$ as classical coulomb energies under various models. The results obtained are in good agreement with the Hartree-Fock estimates.

INTRODUCTION

Density functional theory[1] is basically of electronic ground state structure of atoms, embossed by electronic density distribution $\rho(n)$. Over the past three decades, it has been increasingly useful for understanding and calculation of ground state density $\rho(r)$ and energy[2] (E) of molecules[3] and solids, in other words, any system consisting of nuclei and electrons under applied static perturbations. The utility of DF application lies with quality of density function $\rho(r)$. In this regard, the analytical expression of density function is the simplest way to understand the insight of electronic structure for atoms and molecules.

The present work is devoted to estimating the coulomb energies for first row of atoms under local and non-local approximations. In view of this Pacios[4] partitioned density function has been used under density function formalism. It is seen that the gradient correction to the kinetic energy is necessary for the estimation of these values.

During the past many years there has been a lot of interest in the density functional approach to interpret the chemical and physical properties of atomic and molecular systems in terms of density, and it is highly desirable to use this quantity as a basic variable in quantum chemistry. Yet, no theory has been developed to relate electron density directly to other quantities, like energy, satisfactorily. For this, some kind of approximation has to be made. Some of these lead to the results which are comparable with the Hartree-Fock values in some respects. In many cases they give poor and unphysical results.

Many attempts have been made, using various models, like Thomas-Ferm[5] model and its extension gives considerable insight into the properties of true electronic systems.

The main interest in density-functional description of the electronic structure of an atom is the classical repulsion between electronic charge distribution and itself, given as

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$$J(\rho) = \frac{1}{2}\iint \frac{\rho(1)\,\rho(2)}{r_{12}}\,dr_1\,dr_2 \tag{1}$$

where, ρ is the total electron density for an atom in its ground state. It is also quite interesting to make the approximation to $J(\rho)$ and the equivalent form of equation (1) (already proposed[6] and studied[7] in detail) is the so-called local approximation, given by

$$J_L(\rho) = B_0 M^{2/3} \int \rho^{4/3}(r)\,dr \tag{2}$$

where, B_0 is the universal constant and M the number of electrons.

In the present work, the function selected to represent $\rho(r)$ in a physically meaningful form is a simple sum of exponential terms,

$$\rho(r) = \sum_{i=1}^{M_1} A_i \exp(-B_i r) \tag{3}$$

An energy-density functional with gradient correction upto fourth order in kinetic energy is

$$E(\rho) = T_0(\rho) + T_2(\rho) + T_4(\rho) + V_{ne}(\rho) + V_{ee}(\rho) + K(\rho) \tag{4}$$

where

$$T_0(\rho) = (3/10)\cdot(3\pi^2)^{2/3}\int \rho^{5/3}(r)\,dr$$

$$T_2(\rho) = (1/8)\int (\nabla\rho)^2/\rho\,dr$$

$$T_4(\rho) = p\int\left\{\rho^{1/3}\left(\frac{\nabla\rho}{\rho}\right)^2 - \frac{9}{8}\left(\frac{\nabla\rho}{\rho}\right)^3 + \frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^4\right\}dr$$

where $p = \dfrac{(3\pi^2)^{-2/3}}{540}$.

$$V_{ne}(\rho) = -Z\int \rho(r)\,dr \tag{5}$$

$$V_{ee}(\rho) = 0.4702\int \rho^{4/3}(r)\,dr \tag{6}$$

$$K(\rho) = \beta_1 Z^{2/3}\int \rho^{4/3}(r)\,dr \tag{7}$$

RESULTS AND DISCUSSION

The Pacios energy density function has been used to estimate the classical coulomb energies for first row of atoms and the results are reported here. We have used the following three different energy-density functionals for obtaining the partitioned charge density distributions:

Model-I: An energy-density functional similar to the Thomas-Fermi density (TFD) model[8, 9] (*i.e.* Eqn. (4) without $T_2(\rho)$ and $T_4(\rho)$ terms);

Model-II: Simple TFD model with gradient correction up to second order[10, 11] (*i.e.* Eqn. (4) without $T_4(\rho)$ term);

Model-III: TFD model with gradient correction to kinetic energy upto fourth order[12] (*i.e.*. Eqn. (4)).

The charge density distributions obtained from the use of the above are used to estimate $J_L(\rho)$ and the results of the study are shown in Table-1. For the first row of atoms, the value of constant B_0 is found to be 0.8537 compared with the

values obtained by Bartolotti and Parr[13] being 0.9299. The value obtained from the present work, for the neutral atoms, is 1.20% (standard percentage error) of the actual or Hartree-Fock values, if the use of Eqn. (3) is made. Furthermore, the results are shown in Table-2 when the addition of the first 'gradient correction' to Eqn. (2) is made, giving the so called non-local approximation having the formula of the form

$$J_{NL}(\rho) = BN^{2/3} \int \rho_{(r)}^{4/3}\, dr - CN^{4/3} \int \left(\frac{\nabla \rho}{\rho^{4/3}} \right)^2 dr \qquad (8)$$

where B and C are constants having the values 1.8116 and 0.0064 respectively. The justification of equation (5) is already discussed.[14] By comparing the results of Tables1 and 2, it is interesting to note that the results improve as one goes from Model-1 to Model-III. In the case of F and Ne atoms, Model-I seems to be better (Table-2).

TABLE-1
CLASSICAL COULOMB ENERGY $J_L(\rho)$ (ATOMIC UNITS)
LOCAL APPROXIMATION

At. No.	Model			
	I	II	III	HF[a]
3	4.6	4.0	3.9	4.1
4	8.4	7.7	7.3	7.2
5	14.6	12.7	11.9	11.7
6	20.3	19.1	17.6	17.8
7	28.7	27.5	26.8	26.2
8	42.1	39.9	37.1	36.6
9	54.1	52.5	51.7	50.9
10	71.0	69.3	66.7	66.1

[a] See reference 14.

TABLE-2
CLASSICAL COULOMB ENERGY, $J_{NL}(\rho)$ (ATOMIC UNITS)
NON-LOCAL APPROXIMATION

At. No.	Model			
	I	II	III	HF[a]
3	4.0	3.7	3.7	4.1
4	7.9	7.5	6.9	7.2
5	13.0	11.9	11.5	11.7
6	20.0	19.1	18.0	17.8
7	28.5	27.3	26.2	26.2
8	38.9	37.0	36.1	36.6
9	51.1	50.7	50.1	50.9
10	64.7	60.7	63.7	66.1

[a] See reference 14.

Conclusion

It appears from the present study that the gradient correction to kinetic energy is quite important for the estimation of $J_L(\rho)$ and $J_{NL}(\rho)$ values. Our next theoretical step is to extend this study to the electron density distribution in molecules.

ACKNOWLEDGEMENTS

The author is grateful to Dr. A. Sankara Reddy, Principal, for providing computer facility and encouragement to carry out this work. Further, the author is thankful to her colleagues in the Chemistry Department for their co-operation and help.

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(*Received*: 21 February 1998; *Accepted*: 9 June 1998) AJC-1497