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Momentum Space Properties of Atoms and Molecules

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The determination of structure and properties of biomolecular systems have opened new concepts in chemistry by obtaining accurate electron charge densities. For a long time, the density functional theory has played a major role in predicting the electronic structures of the above systems. In the light of this, the Analytical Model Density (AMD) function proposed by L.F. Pacios has been used to calculate the momentum space properties for representative elements and their combination in molecular form. The results are in good agreement with Hartree-Fock estimates. Further, the cusp condition $\langle \Delta^2\rho\rangle/\langle\rho r^{-1}\rangle$ has been calculated which is vital in assigning the accurate description of electron density at the nucleus.

INTRODUCTION

Density functional theory (DFT)[1, 2] is basically of electronic ground state structure, embossed by electronic density distribution $\rho(r)$. Over the past three decades, it has become increasingly useful for the understanding and calculation of ground state density $\rho(r)$ and energy[3] (E) of molecules, clusters[4] and solids, in other words, any system consisting of nuclei and electrons under applied static perturbations. Further, the crucial issue of DF applications depends on the quality of the description of $\rho(r)$. A number of DF calculations have resorted to numerical procedures to avoid all the undesired deviations typically associated with basis sets. The utility of analytical expressions of density function lies in the simplest way to calculate intrinsic properties of atoms and molecules, which can be further extended to understand the chemical reaction through exothermicity or endothermicity.

In the present work, I have used the analytical model density (AMD) function devised by Pacios[5, 6], which is a very simple representation of Hartree-Fock (HF) atomic densities[7] to calculate the momentum space properties of atoms and molecules.

$$\rho(r) = \sum_{i=1}^{M} A_i \exp(-B_i r) \qquad (1)$$

Long time ago, the Thomas-Fermi method[8] was used to calculate momentum space properties of atoms. This self-consistent electron distribution was employed

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as was also the case in the related calculations of the Dirac-Slater exchange energy of neutral atoms by Scott.[9] The relation between mean momentum $\langle p \rangle$ and Dirac-Slater exchange energy, both proportional to $\int \rho^{4/3}(r)\, dr$ has been emphasized by Pathak and Gadre.[10] They also related $\langle p^{-1} \rangle$ to $\int \rho(r)^{2/3} dr$, which is directly related to an observable, the maximum in the compton profile. Later, Allan and March[11] showed that the same local density for the mean momentum also applies to molecules. The general formula is as follows:

$$\langle p^M \rangle = \frac{3(3\pi^2)^{m/3}}{m+3} \int \rho(r)^{1+m/3}\, dr \tag{2}$$

The mean momentum values for m = –1, 2 and –2 have already been published; the value for m = 3, which in turn, leads to average electron density, has not been reported yet. So by calculating the average electron density $\langle \rho \rangle$, a new energy expression, established by me, is reported here.

Calculations

In the equation (1), if m is taken as 3, then

$$\langle p^3 \rangle = \frac{3(3\pi^2)}{6} \int \rho(r)^2\, dr \tag{3}$$

$$\langle p^3 \rangle = 14.8044 \langle \rho \rangle \tag{4}$$

The integral form in eq. (3) is in fact $\langle \rho \rangle$ shown by Hyman *et al.*[12] which is an experimantally measurable quantity related to the intensity scattered by an element.

The new energy expression based on mean momentum for atoms is,

$$E = \frac{\langle p^3 \rangle}{2Z}$$

$$= 14.8044 \langle \rho \rangle / 2Z \qquad 2Z = \text{atomic number}$$

Earlier Ray and Tandon[13] have shown a very good correlation between $\langle \rho \rangle$ and E, and for molecules, the expression is given below.

$$E_{mol} = \frac{\langle p^3 \rangle}{2 \sum_{i=1}^{M} Z_i} \tag{6}$$

By extending this idea, the results for the cusp condition is also reported, in the form of mean momentum values, as $\langle r^{-1}\rho \rangle$, $\langle r^{-2}\rho \rangle$, $\langle \Delta^2 \rho \rangle$.

The respective simplified forms for various expressions mentioned above are

$$\langle r^{-1}\rho \rangle = 4\pi \left[\frac{A_1^2}{(2\beta_1)^2} + \frac{A_2^2}{(2\beta_2)^2} + \frac{2A_1A_2}{(\beta_1+\beta_2)^2} \right] \tag{7}$$

$$\langle r^{-2}\rho \rangle = 4\pi \left[\frac{A_1^2}{2\beta_1} + \frac{A_2^2}{2\beta_2} + \frac{2A_1A_2}{(\beta_1+\beta_2)} \right] \tag{8}$$

$$\langle \nabla^2 \rho \rangle = 4\pi \left[\frac{A_1^2}{4\beta_1} + \frac{A_2^2}{4\beta_2} + \frac{2A_1A_2(\beta_1^2 + \beta_2^2)}{(\beta_1 + \beta_2)^3} \right] \quad (9)$$

The cusp condition, by definition, is

$$\left. \frac{\partial \rho(r)}{\partial r} \right|_{r=0} = -2Z\rho(0) \quad (10)$$

The new cusp condition results worked out in the present work, on the basis of momentum space, are

$$\langle \nabla^2 \rho \rangle / \langle r^{-1} \rho \rangle = 2Z \quad (11)$$

$$\langle r^{-2} \rho \rangle / \langle r^{-1} \rho \rangle = 4Z \quad (12)$$

From equations (11) and (12),

$$\langle r^{-2} \rho \rangle / \langle \Delta^2 \rho \rangle = 2 \quad (13)$$

RESULTS AND DISCUSSION

The density functional calculations have been reported by using AMD for various properties based on momentum space. It can be seen from Table-1 that the mean momentum energy values are in good agreement with Hartree-Fock values. The error in terms of percentage is ±3.0.

TABEL-1
MEAN MOMENTUM ENERGIES FOR ATOMS (a.u.)

Atom	$\langle \rho \rangle$	E_{cal}	E_{HF}^{a}
Li	3.15	7.52	7.43
Be	8.34	15.10	14.57
B	17.39	25.21	24.52
C	31.92	38.02	37.68
N	51.81	54.51	54.40
O	79.92	74.20	74.81
F	117.76	98.50	99.41
Ne	166.73	126.70	128.54

[a] See Reference 7.

Recently, in one of his papers, Pacios put forward the idea of using partitioned density function for molecules, but no results along this line have been reported. So I tried to extend this work to molecules on the basis of the assumption adopted by Zanasi and Lazzeretti.[14] Their approach was based on the assumption that in some manner, it is possible to resolve the electron density in the multi-centre molecular problem into the sum of atomic-like localized electron density functions. The results have been reported in Table-2. It is interesting to note that the calculated values by AMD are in good agreement with HF. Though the results obtained for simple molecular systems are not very encouraging but by modifying

the density function with some physically significant parameters, this can be improved.

TABLE-2
MEAN MOMENTUM ENERGIES FOR MOLECULES (a.u.)

System	$\langle\rho\rangle_M$	E_{Cal}	E^a_{HF}
OH	81.1956	66.7800	—
HF	119.0828	88.1500	100.0
HCl	995.4027	409.3428	—
CH	32.3084	34.1647	—
NH	52.8255	48.8781	—
PH	643.1526	297.5465	—
CO	208.5857	110.2857	112.7
LiH	3.6598	6.7726	—
BF	217.1896	114.8345	124.2
BeH_2	9.7950	12.0841	—
H_2O	73.7381	54.5824	76.1

[a] See Reference 15.

TABLE-3
CUSP CONDITION, EQUATIONS 11 AND 12, FOR THE AMD

System	$\langle\Delta^2\rho\rangle$	$\langle r^{-1}\rho\rangle$	$\langle r^{-2}\rho\rangle$	$\frac{\langle r^{-2}\rho\rangle}{\langle\nabla^2\rho\rangle}$	$\frac{\langle\nabla^2\rho\rangle}{\langle r^{-1}\rho\rangle}$	Cusp[a]
Li	104.11	17.94	207.04	1.99	5.80	5.80
Be	505.51	64.29	1003.42	1.98	7.86	7.86
B	1660.01	167.09	3284.57	1.98	9.93	9.94
C	4333.85	360.71	8542.33	1.97	12..01	12.03
N	9698.48	688.01	19039.38	1.96	14.10	14.12
O	19423.45	1200.73	37974.40	1.96	16.18	16.22
F	35771.43	1960.01	69648.54	1.95	18.25	18.33
Ne	61695.49	3036.52	119632.09	1.94	20.32	20.45
Na	100774.08	4434.09	193402.32	1.98	22.73	—
Mg	157686.29	6336.37	302011.97	1.99	24.89	—
Al	241600.43	8941.11	459541.90	1.98	27.02	—
Si	357675.63	12374.71	680721.32	1.97	28.90	—
P	513250.74	16582.72	974447.03	1.96	33.25	—
S	718230.67	21724.70	1359046.70	1.96	33.06	—
Cl	983632.58	27932.81	1853664.00	1.95	35.21	—

[a] See reference 6.

For any molecule, its electronic structure requires that it should satisfy the cusp condition, which is important to understand the electron density at the nucleus. In view of this, the mean momentum values can be used to check it. The results are reported in Table-3. It can be seen from the comparison that from Li to Cl elements the value of the cusp is very close to 2.0. This is a new concept by which the cusp can be understood through momentum space.

Conclusion

The present study opens a new chapter in understanding the electronic concepts of atoms and molecules through momentum space. My next step in this direction will be to calculate the heat of formation of chemical reactions by using mean momentum expression.

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