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Citation: *The Journal of Chemical Physics* **83**, 239 (1985); doi: 10.1063/1.449814

View online: <http://dx.doi.org/10.1063/1.449814>

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Local density approximations to moments of momentum of diatomic molecules with Hartree-Fock-Roothaan quality electron distributions

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(Received 13 September 1984; accepted 17 December 1984)

By generalizing local density arguments for atoms it is found that the m th moment of momentum for molecules $\langle p^m \rangle$ is proportional to $\int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$, where $\rho(\mathbf{r})$ is the electron density. This relation is tested for $m = -1, 1$, and 2 using wave functions of Hartree-Fock-Roothaan quality: $\langle p^m \rangle$ is computed directly and the density integrals are evaluated using $\rho(\mathbf{r})$ generated from these wave functions. Eleven neutral diatomic systems and two singly charged positive ions are considered. Apart from changes in the proportionality constants, the local density approximation is vindicated; for $m = -1, 1$, and 2 the magnitudes of the changes in the predicted constants are less than $\sim 10\%$. Finally, $\langle p \rangle$, which is proportional to the Dirac-Slater exchange energy, is compared with the appropriate self-consistent Hartree-Fock-Roothaan energy terms and, again, a linear relationship emerges.

A long time ago, the Thomas-Fermi method, which is the simplest version of modern density functional theory,¹ was used to calculate momentum space properties of atoms. In such work² the self-consistent Thomas-Fermi electron distributions were employed, as was also the case in the related calculations of the Dirac-Slater exchange energy of neutral atoms by Scott.³ The relation between mean momentum $\langle p \rangle$ and Dirac-Slater exchange energy, both proportional to $\int \rho(\mathbf{r})^{4/3} d\mathbf{r}$ where $\rho(\mathbf{r})$ is the electron density, has been emphasized more recently by Pathak and Gadre.⁴ They also related $\langle p^{-1} \rangle$ to $\int \rho(\mathbf{r})^{2/3} d\mathbf{r}$; in turn, $\langle p^{-1} \rangle$ is directly related to an observable, namely the maximum in the Compton profile.

Subsequently, Allan and March⁵ showed that the same local density formula for the mean momentum also applies to molecules. A straightforward extension of their argument leads to

$$\langle p^m \rangle = \frac{3(3\pi^2)^{m/3}}{m+3} \int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r} \quad (1)$$

in atomic units, which we use throughout. Extending previous work⁴ on atoms for $m = +1$, the purpose of the present article is to report calculations of both sides of the local density approximation [Eq. (1)] using wave functions of Hartree-Fock-Roothaan quality. All the wave functions were computed using the same $9s/6p/3d$ universal even-tempered Slater-type orbital basis set.⁶ The left-hand side of Eq. (1) was evaluated via the Fourier transform of $\psi(\mathbf{r})$ and the right-hand side was determined straightforwardly from $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$.

Plots of $\langle p^m \rangle$ against $\int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$ are shown in Fig. 1 for $m = -1, 1$, and 2 for eleven neutral diatomics and two singly charged positive molecular ions. For convenience the values of $\langle p^m \rangle$ and $\int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$, are also collected together in Table I. The linear relation predicted by Eq. (1) is obeyed in each case; the observed

slopes are compared with the predicted proportionality constants in Table II. The quantitative agreement with the local density prediction is evidently best for $m = 1$, although the other numerical slopes only differ from the predictions by 7%–10%. The scatter around the straight

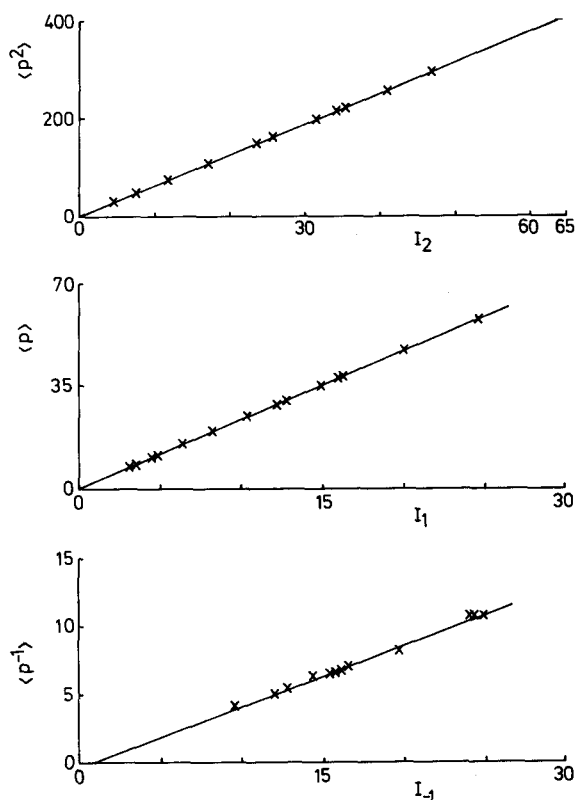


FIG. 1. $\langle p^m \rangle$ as calculated from Hartree-Fock-Roothaan wave functions plotted against $\int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$, with $\rho(\mathbf{r})$ calculated from the same wave functions, for three cases $m = -1, 1$, and 2 . Slopes of linear plots are recorded in Table II.

TABLE I. Values of $I_m = \int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$, $\langle p^m \rangle$ and (for closed shells only) the exchange energy for the systems studied. Each system was in its ground electronic state. The bond lengths used are given in Bohr.

System	I_2	$\langle p^2 \rangle$	I_1	$\langle p \rangle$	I_{-1}	$\langle p^{-1} \rangle$	$\sum_{i,j}^n K_{ij}$
Be	4.573	29.146	3.131	7.434	14.475	6.324	2.667
BeH ⁺ (2.124)	4.753	30.081	3.420	8.072	9.687	4.210	2.916
BeH (2.537 1)	4.746	30.302	3.589	8.585	16.148	6.606	
BH ⁺ (2.295 44)	7.741	49.567	4.580	11.026	12.095	5.061	
BH (2.350 1)	7.881	50.240	4.898	11.682	16.661	7.098	4.129
CH (2.124)	11.962	76.507	6.446	15.508	16.596	6.876	
NH (2.0)	17.186	109.833	8.280	19.911	16.181	6.709	
OH (1.834 2)	23.727	150.760	10.410	24.853	15.842	6.584	
LiO (3.203 07)	25.917	164.588	12.238	29.120	19.782	8.139	
HF (1.834 2)	31.731	199.842	12.817	30.304	15.537	6.517	10.399
N ₂ (2.124)	34.267	217.210	15.983	37.939	24.388	10.760	13.061
CO (2.124)	35.619	225.329	16.307	38.639	24.186	10.687	13.334
Ne	41.019	257.094	14.939	35.197	12.893	5.453	12.108
O ₂ (2.282)	47.084	298.18	20.018	47.668	24.640	10.699	
F ₂ (2.75)	62.961	398.87	24.643	58.428	24.998	10.783	19.911

TABLE II. Numerical slopes of $\langle p^m \rangle$ vs $\int \rho(\mathbf{r})^{1+(1/3)m} d\mathbf{r}$ compared with the predictions of Eq. 1.

m	$\frac{3(3\pi^2)^{m/3}}{m+3}$	Numerical slope ^a α_1	Numerical slope ^b α_2	Intercept ^b β_2
-1	0.48	0.43	0.45	-0.40
1	2.32	2.37	2.37	0.11
2	5.74	6.33	6.33	0.51

^a Data fitted to $\langle p^m \rangle = \alpha_1 I_m$.

^b Data fitted to $\langle p^m \rangle = \alpha_2 I_m + \beta_2$.

line is somewhat larger for $m = -1$ than for the other plots.

Having vindicated the local density approximation for a series of light diatomic species, we again generalize the considerations of Pathak and Gadre⁴ to molecules. We relate $\langle p \rangle$, and hence also the Dirac–Slater exchange energy, to the appropriate self-consistent Hartree–Fock–Roothaan energy terms. Although exchange interactions are restricted to pairs of electrons of the same spin, it is more convenient for closed-shell configurations to write the two-electron contribution to the total energy as

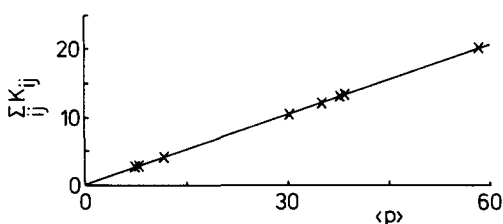


FIG. 2. $\sum_{i,j}^n K_{ij}$ vs $\langle p \rangle$.

$$\sum_{i,j=1}^n (2J - K)_{ij},$$

where n is the number of doubly occupied orbitals; \mathbf{J} and \mathbf{K} are Coulomb and exchange matrices, respectively. In Fig. 2 we show that a plot of $\sum_{i,j} K_{ij}$ vs $\langle p \rangle$ is a good straight line. For closed-shell systems the values of $\sum_{i,j} K_{ij}$ are given in the last column of Table I.

In summary, even for the light diatomics considered here, the local density approximation embodied in Eq. (1) is notably successful for the cases $m = -1$, 1, and 2 that we treated. Changes in the proportionality constants of $\sim 10\%$ or less lead to fully quantitative agreement between fully wave mechanical calculations of moments of momentum and the corresponding local density approximations.

One of us (N.L.A.) wishes to acknowledge the award of a postgraduate studentship from SERC during the course of this work. D.L.C. thanks the Royal Society for a Research Fellowship, and SERC for computer time at RAL.

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