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The gradient expansions of the kinetic energy and the mean momentum for light diatomic molecules

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For eleven neutral diatomic systems and one positive ion we have numerically evaluated the three terms in the gradient expansion of the molecular kinetic energy $T = T_0 + T_2 + T_4$. Hartree-Fock-Roothaan molecular densities were used throughout. For the molecules studied $T_2/T_0 \sim 0.1$, $T_4/T_2 \sim 0.2$. The contributions to these integrals from different regions of space were examined. We have also estimated the values of the two terms in the gradient expansion of the mean momentum $P = P_0 + P_2$ and find $P_2/P_0 \sim 0.5$. Lastly we make contact with earlier work of Mucci and March. D/N^2 is found to correlate grossly with T_2 , where D is the dissociation energy and N the total number of electrons in the molecule.

I. INTRODUCTION

There has been recent interest in the electron density gradients.¹⁻³ In particular the work of Wang *et al.*¹ on the gradient expansion of the atomic kinetic energy functional has prompted us to study this expansion and that of the mean momentum for a set of light diatomic molecules using Hartree-Fock-Roothaan molecular densities $\rho(\mathbf{r})$. Specifically for the kinetic energy,

$$T = T_0 + T_2 + T_4, \quad (1.1)$$

where

$$T_0 = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(\mathbf{r})^{5/3} d\mathbf{r}, \quad (1.2)$$

$$T_2 = \frac{1}{72} \int \frac{(\nabla \rho)^2}{\rho} d\mathbf{r}, \quad (1.3)$$

$$T_4 = \frac{1}{540(3\pi^2)^{2/3}} \int \rho^{1/3} \left\{ \left(\frac{\nabla^2 \rho}{\rho} \right)^2 - \frac{9}{8} \left(\frac{\nabla^2 \rho}{\rho} \right) \left(\frac{\nabla \rho}{\rho} \right)^2 + \frac{1}{3} \left(\frac{\nabla \rho}{\rho} \right)^4 \right\} d\mathbf{r}. \quad (1.4)$$

Our gradient expansion of T is identical to that used by Wang *et al.*¹ and we follow them and use the correction due to Hodges.⁴ There are two nondivergent terms in the gradi-

ent expansion of the mean momentum P ,³

$$P = P_0 + P_2, \quad (1.5)$$

$$P_0 = \frac{3(3\pi^2)^{1/3}}{4} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}, \quad (1.6)$$

$$P_2 = \frac{1}{72(3\pi^2)^{1/3}} \int \frac{(\nabla \rho)^2}{\rho^{4/3}} d\mathbf{r}. \quad (1.7)$$

For comparison the Hartree-Fock mean momentum $\langle p \rangle$ was evaluated via the Fourier transform of $\psi(\mathbf{r})$.

The outline of the paper is as follows. Section II reports the evaluation of T_0 , T_2 , and T_4 as defined by Eqs. (1.2)–(1.4). In section III we examine the values of P_0 and P_2 . Lastly we test in Sec. IV the proposals of Mucci and March² and a correlation between T_2 and D/N^2 is established. Here D is the molecular dissociation energy and N is the total number of electrons in the molecule.

II. EVALUATION OF T_0 , T_2 , and T_4

The electron density $\rho(\mathbf{r})$, its gradient $\nabla \rho$, and the Laplacian $\nabla^2 \rho$ were evaluated for eleven neutral diatomic systems and one positive molecular ion BH^+ using wave functions of Hartree-Fock-Roothaan quality. All the wave functions were computed using the same $9s/6p/3d$ universal basis set on each atom⁵ as in previous work.⁶

TABLE I. Values in a. u. of T_0 , T_2 , T_4 , $T = T_0 + T_2 + T_4$, and $T_m = T_0 + T_2 + 0.5T_4$. The Hartree-Fock kinetic energy for the molecules studied, T_{HF} is also given. All molecules were in their ground electronic states; the bond lengths are given in Bohrs.

Molecule	T_0	T_2	T_4	T	T_m	T_{HF}
$\text{BH}^+(2.29544)$	22.23	2.48	0.50	25.21	24.97	24.784
$\text{BeH}(2.5371)$	13.63	1.56	0.31	15.50		15.151
$\text{BH}(2.3501)$	22.63	2.50	0.49	25.62		25.120
$\text{CH}(2.124)$	34.35	3.59	0.70	38.64	38.30	38.254
$\text{NH}(1.9581)$	49.38	4.89	0.95	55.22	54.76	54.949
$\text{OH}(1.8342)$	68.13	6.40	1.25	75.78	75.17	75.380
$\text{HF}(1.7325)$	91.24	8.12	1.58	100.9	100.2	100.07
$\text{LiO}(3.203\ 07)$	74.41	7.14	1.39	82.94	82.27	82.294
$\text{CO}(2.1322)$	102.2	9.82	1.91	113.9	113.0	112.64
$\text{N}_2(2.068)$	98.58	9.60	1.87	110.1	109.1	108.79
$\text{O}_2(2.282)$	135.2	12.7	2.45	150.4	149.2	149.43
$\text{F}_2(2.680)$	180.6	16.2	3.12	199.9	198.4	198.57

TABLE II. Contributions to T_0 , T_2 , and T_4 for N_2 , with a bond length 2.068 Bohr. Distances are measured from the center of the bond, $R\theta = 1.034$ Bohr, with the coordinate system defined in Sec. II.

Range (a.u.)	Value of integral over range		
	T_0	T_2	T_4
0.0–0.9	7.41	0.93	0.045
0.9– $R\theta$	37.44	3.23	0.831
$R\theta$ –1.1	26.46	2.02	0.751
1.1–2.0	26.01	3.19	0.212
2.0–4.0	1.259	0.233	0.013
4.0–10.0	1.77×10^{-3}	7.18×10^{-3}	0.018
10.0–20.0	2.3×10^{-12}	3.1×10^{-8}	3.1×10^{-4}
20.0–30.0	2.8×10^{-18}	1.0×10^{-11}	2.5×10^{-5}

The values of T_0 , T_2 , and T_4 are collected together in Table I. $T_2/T_0 \sim 0.1$, $T_4/T_2 \sim 0.2$ for all the molecules studied, a result similar to that discussed by Wang *et al.*¹ for the He and Ne atoms. Table II shows the contributions from various regions to T_0 , T_2 , and T_4 for the typical case of N_2 . We have used spherical coordinates and the ranges given define annuli centered at the midpoint of the bond. Beyond 10 a.u. from the center of the molecule, there is no significant contribution to T_0 or T_2 . We have also found that major contributions from regions very close to the nuclei are relatively more important for T_4 than for T_0 or T_2 .

Also recorded in Table I are the Hartree–Fock kinetic energies T_{HF} . $T_0 + T_2$ is within 1.2% of T_{HF} for all the molecules studied. For the two lightest neutral molecules, BeH and BH, $T_0 + T_2$ gives an overestimate of T_{HF} ; for the remainder $T_0 + T_2$ is an underestimate. $T_0 + T_2 + T_4$ is an overestimate for all the molecules.

Thus far there has not been a definitive derivation of T_4 . For example, the derivations due to Hodges⁴ and to Kirzhnits⁷ make different underlying assumptions and the Kirzhnits correction $T_4^{(K)}$ is related to the Hodges correction $T_4^{(H)}$ by $T_4^{(H)} = -\frac{1}{3}T_4^{(K)}$. We therefore thought it useful to follow the suggestion of Wang *et al.*¹ and investigate modified functionals of the form $T_m = T_0 + T_2 + \gamma T_4$. For the molecules for which $T_0 + T_2$ is an overestimate, a least-square fit of the data yields $\gamma = 0.5$ and this modification gives values for T_m

TABLE III. Values (in atomic units) of the terms in the gradient expansion for the mean momentum, and the Hartree–Fock mean momentum, for the molecules studied.

Molecule	P_0	P_2	$P_0 + P_2$	$P_0 + 0.54P_2$	$\langle p \rangle$
BH ⁺	10.63	0.700	11.33	11.00	11.026
BeH	8.327	0.566	8.893	8.63	8.585
BH	11.37	0.712	12.08	11.75	11.682
CH	14.96	0.833	15.79	15.41	15.508
NH	19.24	0.967	20.21	19.73	19.935
OH	24.15	1.01	25.16	24.70	24.853
HF	29.74	1.26	31.00	30.42	30.304
LiO	28.40	1.40	29.80	29.15	29.120
CO	37.82	1.75	39.57	38.78	38.625
N ₂	37.19	1.74	38.93	38.02	38.032
O ₂	46.45	2.04	48.49	47.55	47.668
F ₂	57.18	2.39	59.57	58.47	58.396

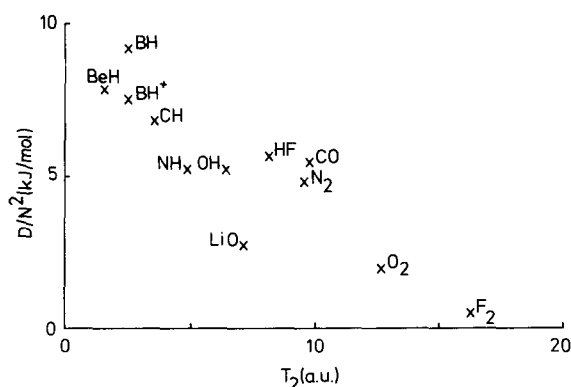


FIG. 1. D/N^2 vs T_2 for the molecules studied.

that agree with T_{HF} typically within 0.4% and at worst to within 0.7%. These values of T_m are also given in Table I.

III. EVALUATION OF P_0 and P_2

Values of the exact mean momentum $\langle p \rangle$, and P_0 and P_2 evaluated using Eqs. (1.6) and (1.7) are given in Table III. $P_2/P_0 \sim 0.05$, which contrasts with $T_2/T_0 \sim 0.1$. $P_0 + P_2$ is an overestimate of $\langle p \rangle$ for all the molecules studied. We list also the values of the modified functional $P_0 + \gamma P_2$ with $\gamma = 0.54$ (obtained from a least-squares fit) which gives values for P which agree with $\langle p \rangle$ to within 0.9% at the very worst.

IV. DISSOCIATION ENERGIES OF DIATOMICS RELATED TO ELECTRON DENSITY GRADIENTS

Lastly we explore and extend the proposals of Mucci and March.² They suggest that the dissociation energies of diatomic molecules may be characterized by T_2 on the basis of Teller's theorem⁸ which states that molecular binding cannot occur in any local electron density theory which neglects electron density gradients.

We have found that D/N does not correlate with T_2 , and the reported correlation in Ref. 2 resulted from the limited range of molecules considered and was somewhat fortuitous. Further, and more surprisingly, there is no correlation with the force constant (a measure of the binding in the equilibrium configuration). However, inspired by Ref. 2 we plot D/N^2 vs T_2 in Fig. 1. Bearing in mind the substantial variation in ionicity through the range of diatomics studied, there is a considerable degree of correlation between these quantities. However, in the light of experience, full theoretical analysis of this relationship is needed before this correlation can be taken as definitive. We should caution that it is not claimed that T_2 , essentially a property of the equilibrium molecular electron density, can lead to an absolute determination of D .

V. CONCLUSION

A truncated gradient expansion has been found to give accurate values of the kinetic energy and the mean momentum for the light diatomic systems studied. At present we are investigating the changes in T_0 and T_2 with internuclear sep-

aration to see if such expansions, using Hartree-Fock densities or better, are useful beyond revealing gross trends in the Periodic Table.

There seems to be a marked correlation between D/N^2 and T_2 for the molecules considered here. We feel it will be worthwhile to extend the present work to heavier molecules. In such an extension, it may be illuminating to consider homonuclear and heteronuclear diatomics separately as there are reasons for expecting significantly different behavior for D as a function of N in the two cases as N increases.⁹

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