

Density-gradient expansion of the kinetic-energy functional for molecules

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The gradient expansion of the molecular kinetic-energy functional is assessed through numerical results for 14 diatomic and polyatomic molecules. The correlation of the dissociation energies (D_e) of molecules with the Weizsacker contribution to the kinetic energy (T_W) is established through a plot of D_e/N^2 against T_W where N is the number of electrons. The conclusions support and extend the observations of Allan *et al.* [J. Chem. Phys. **83**, 4562 (1985)]

Results on the density-gradient expansion of the kinetic-energy functional, $T[\rho] = T_0 + T_2 + T_4$, for molecular systems have been reported only recently by Allan *et al.*¹ although analogous studies for atoms have been quite extensive.² For light diatomic molecules, Allan *et al.* have assessed the gradient expansion functional by numerical comparison with corresponding Hartree-Fock values; they have also verified an earlier conjecture of Mucci and March³ on the correlation between the dissociation energies D_e and the Weizsacker contribution T_W ($T_W = 9T_2$). The present work reports similar investigations for polyatomic molecules and a few diatomic molecules.

In Table I, numerical results for T_0 , $T_0 + T_2$, and $T_0 + T_2 + T_4$, calculated with densities from the double- ζ Gaussian basis wave function of Snyder and Basch,⁴ are compared with the corresponding Hartree-Fock kinetic energies, T_{HF} , for 14 molecules. The ratios of T_2/T_0 and T_4/T_2 are close to 0.1 and 0.2, respectively; $T_0 + T_2$ is found to underestimate T_{HF} by less than 1% for all the molecules except H_2 and BH_3 , while $T_0 + T_2 + T_4$ shows overestimation by more than 1%. The deviation is much reduced if the T_4 term is multiplied by a factor of $\frac{1}{2}$ or $\frac{1}{3}$. Our conclusions are thus essentially the same as those of Allan *et al.*¹ based on the results for diatomic molecules alone.

Allan *et al.*¹ used a Slater basis set whereas we have em-

ployed Gaussian basis set throughout. This enables us to test the sensitivity of the results to the nature of the basis set, since the diatomic molecules HF, CO, N_2 , and F_2 of Table I are molecules also considered by Allan *et al.*¹ It is observed that the T_0 values differ by less than 0.05%, the T_2 's by 0.1%, and the T_4 's by about 3%. This increasing trend may be a consequence of the fact that gradients are more sensitive to the nature of the basis set.

For the molecule N_2 , the local behavior of the kinetic-energy density $t(\mathbf{r}, \rho)$ is displayed in Fig. 1, which is a plot of the z -direction-averaged kinetic-energy density $t_R(R)$ [$= 2\pi \int t(\mathbf{r}, \rho) dz$] (where \hat{z} is the bond axis) against R , the distance from the bond axis. Locally the kinetic-energy components deviate from the Hartree-Fock result; the good global value is a consequence of cancellation of errors in different regions. The shell structure apparent from the piecewise linear nature of $\log_{10} t_R$ is more prominent in the radial density $P_R(R)$ defined as $P_R(R) = 2\pi R \int \rho(\mathbf{r}) dz$, representing the total density in a cylindrical shell at a distance R around the bond axis.

Based on the prediction of the relation between the dissociation energy and the density gradient by Mucci and March,³ Allan *et al.*¹ have shown, for diatomic molecules, a numerical evidence for the correlation between D_e/N^2 (where N is the number of electrons) and the second gra-

TABLE I. Kinetic energies for molecules. Quantities in parentheses indicate relative errors, in percentage with respect to Hartree-Fock values. All values are in atomic units.

Molecule	T_{HF}	T_0	T_W	$T_0 + T_2$	$T_0 + T_2 + T_4$
H_2	1.128	0.981	1.128	1.107 (-1.88)	1.178 (4.44)
BH_3	26.34	23.83	22.99	26.38 (0.17)	26.94 (2.29)
CH_4	40.17	36.45	32.82	40.10 (-0.19)	40.91 (1.85)
HF	100.0	91.30	73.05	99.42 (-0.59)	101.0 (1.00)
NH_3	56.16	50.97	44.22	55.88 (-0.49)	56.90 (1.32)
H_2O	76.08	69.19	57.74	75.61 (-0.62)	76.92 (1.11)
BF	124.2	113.2	94.15	123.7 (-0.41)	125.8 (1.30)
CO	112.7	102.2	88.48	112.1 (-0.52)	114.1 (1.28)
C_2H_2	76.70	69.52	62.98	76.52 (-0.25)	77.93 (1.60)
N_2	108.7	98.53	86.52	108.1 (-0.54)	110.1 (1.25)
H_2CO	113.8	103.3	88.95	113.2 (-0.54)	115.3 (1.30)
F_2	198.5	180.6	145.9	196.8 (-0.85)	199.9 (0.66)
CO_2	187.5	170.3	144.7	186.42 (-0.60)	189.5 (1.05)
N_2O	183.6	166.7	142.8	182.5 (-0.59)	186.2 (1.38)

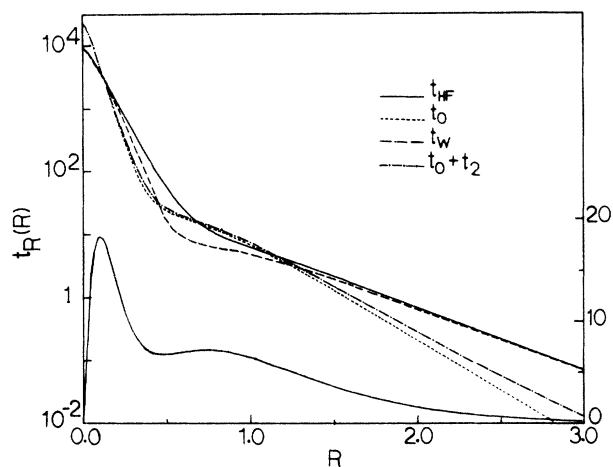


FIG. 1. z -direction-averaged kinetic-energy density $t_R(R)$ [$= 2\pi \int t(\mathbf{r}, \rho) dz$] for the nitrogen molecule vs the distance R from the bond (upper finger). Also z -direction-averaged radial-density $P_R(R)$ [$= 2\pi R \int \rho(\mathbf{r}) dz$].

dient term T_2 . Our plot of D_e/N^2 against T_W , in Fig. 2, for several diatomic and polyatomic molecules shows a very good correlation (almost linear) between these two quantities and thus strengthens the previous conclusion.¹

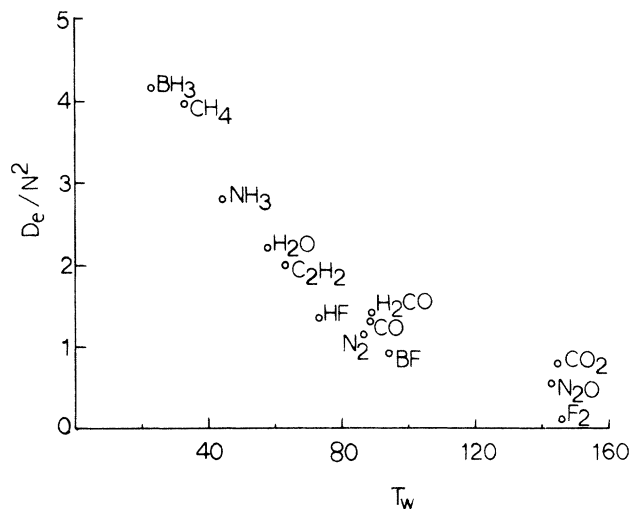


FIG. 2. D_e (in kcal/mol)/ N^2 vs T_W for molecules.

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