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Comments on the correlation between the Weizsäcker correction and the binding energy of diatomic molecules

B. M. Deb and P. K. Chattaraj

Theoretical Chemistry Group, Department of Chemistry, Panjab University, Chandigarh-160 014, India

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Using the double-zeta wavefunctions of Snyder and Basch [5], the Weizsäcker correction $T_w = \frac{1}{8}\int d\vec{r}(\nabla\rho \cdot \nabla\rho)\rho^{-1}$ has been evaluated for the molecules H_2, HF, BF, N_2 and CO. There was no linear correlation between T_w and the binding energy for these molecules.

Key words: Weizsäcker correction — Binding energy — Diatomic molecules

Ever since Balàzs [1] proved that the Weizsäcker correction, $T_w = \frac{1}{8}\int d\vec{r}(\nabla\rho \cdot \nabla\rho)\rho^{-1}$, in the Thomas-Fermi theory is a *necessary* condition for binding in diatomic molecules, interest was centered on the question whether this correction, or a fraction thereof, is *sufficient* to yield the actual binding energy. In case this sufficiency is valid, then there is the interesting possibility of modeling the chemical bond in terms of the electron density $\rho(\vec{r})$ and the gradient density $\nabla\rho$ at only *one* internuclear distance (R_{eq}), instead of the other approaches which require one to study a number of internuclear distances around R_{eq}.

In 1971, Yonei [2] reported a good binding energy (6% error) for the N_2 molecule, using the Thomas-Fermi-Dirac model with $T_w/5$. However, Wang and Parr [3] advocated the use of $T_w/9$, a suggestion that is now generally accepted. Recently, for N_2, HF, BF and F_2, Mucci and March [4] showed a linear correlation between the dissociation energy per electron and a quantity which could be argued to be equal in magnitude to $T_w/9$, *provided* certain higher-order gradient corrections are neglected and the chemical potential (the Lagrange multiplier μ) is taken to be the same as the HOMO energy in the Hartree-Fock theory.

In view of this linear correlation and also because of the inclusion of F_2 in it, we decided to directly calculate T_w for H_2, HF, BF, N_2 and CO, using the double-zeta wavefunctions of Snyder and Basch [5]; F_2 was not chosen since for this molecule the wavefunction concerned does not give binding. Since this is probably the first reported calculation of Weizsäcker correction for a series of molecules (apart from Yonei's [2] calculations on N_2) we describe below how the integral T_w was evaluated:

1. For every molecule, the coordinate origin was that chosen by Snyder and Basch [5]. Since the double-zeta basis set consists of contracted Gaussians, at first the cartesian coordinates were transformed to spherical polar ones. Next, in view of the azimuthal symmetry of linear molecules, the integration over $0 \le \phi \le 2\pi$ was performed analytically. The remaining integration over r and θ was then performed numerically, using Gauss-Legendre quadrature for both.
2. Since both ρ and $\nabla\rho$ predominate in a relatively small range around the origin and die away exponentially at larger distances, a square mesh was chosen for the sub-intervals for r-integration, i.e.,

$$r = x^2, \qquad x_{i+1} = x_i + h.$$

In each sub-interval, x changes with uniform step size h, starting from zero in the first sub-interval.
3. For θ-integration, sub-intervals of equal length were chosen between 0 and π.
4. In each sub-interval, for either r- or θ-integration, a four-point Gauss-Legendre formula was used. For testing the stability of results, the number of sub-intervals in r and θ was increased and h (in case of r) was decreased. Results were found to oscillate around the exact value, the amplitude of oscillation decreasing with increasing number of sub-intervals and decreasing h. With an increase in the number of electrons N in a molecule, the number of sub-intervals in r and θ increases while h decreases, for final stable results. For the isoelectronic molecules N_2, BF and CO, the value of h and the number of sub-intervals in r and θ are, respectively: 0.12, 25, 6; 0.12, 20, 6; 0.1, 20, 6.
5. The normalization condition, $\int\rho(\vec{r})\,d\vec{r} = \mathrm{N}$, was always maintained. All calculations were in single precision. For comparison, the correction term

$$T_r = -\tfrac{1}{40}\int d\vec{r}(\vec{r}\cdot\nabla\rho)r^{-2},$$

proposed by Haq et al. [6], was also numerically evaluated, following the above procedure, since it was shown [6] that T_r is also a necessary condition for chemical binding in diatomic molecules.

Table 1 reports the values of various kinetic-energy terms along with the normalization and dissociation-energy (D) values. Figures 1 and 2 depict plots of D and D/N against T_w and T_r respectively. From these we see that there is no evidence of any linear relationship. On the other hand, a plot (Fig. 3) of D against either T_w/N or $\log(T_w/N)$ yields the semblance of a straight line embracing N_2, BF

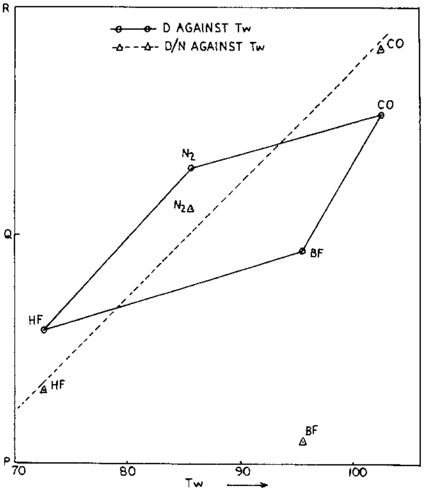

Fig. 1. Plot of D (*solid line*) and D/N (*dotted line*) against T_w, in atomic units. Values of P, Q, R respectively are: D-plot, 0.1, 0.3, 0.5; D/N-plot, 0.02, 0.025, 0.03. The H_2 molecule is not shown

and HF, but excluding H_2 and CO, which superficially looks like the Mucci-March plot. Similarly, a plot of D/N against log T_w gives a straight line (Fig. 4) embracing HF, N_2 and CO, but excluding H_2 and BF. There does not appear a way of making H_2 fall on such lines. Obviously, such relationships cannot be taken seriously.

A relative comparison between $T_w/9$ and T_r is worth making. For spherically symmetric systems, and with a larger number of electrons, T_r leads to a better value of electronic kinetic energy than $T_w/9$ [6]. However, comparing columns 6, 7 and 8 of Table 1, as well as Figs. 1 and 2, there does not seem to be much

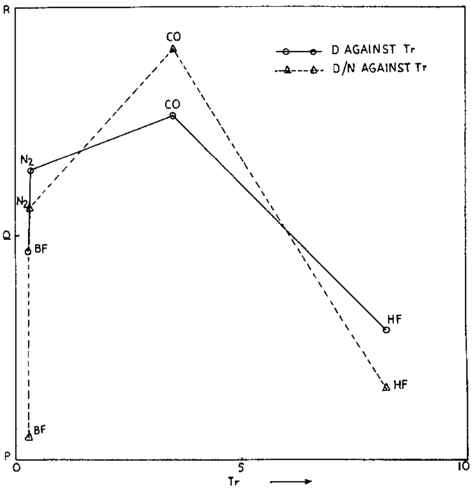

Fig. 2. Plot of D(*solid line*) and D/N (*dotted line*) against T_r, in atomic units. Values of P, Q, R respectively are: D-plot, 0.1, 0.3, 0.5; D/N-plot, 0.02, 0.025, 0.03. The H_2 molecule is not shown

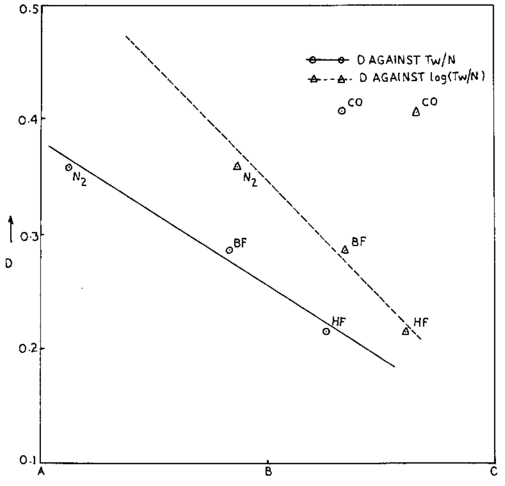

Fig. 3. Plot of D against T_w/N (*solid line*) and against $\log(T_w/\mathrm{N})$ (*dotted line*), in atomic units. Values of A, B, C respectively are: T_w/N-plot, 6, 7, 8; $\log(T_w/\mathrm{N})$-plot, 0.7, 0.8, 0.9. The H_2 molecule is not shown

choice between the two kinetic energy corrections, in the case of linear molecules. An angle-dependent correction to T_r would be worth consideration.

Thus, we conclude that although both T_w and T_r give rise to chemical binding, the calculation of actual binding energy from them, by using a given $\rho(\vec{r})$, is by no means a straight-forward task. The Mucci-March correlation [4] cannot be applied to T_w, because of the presence of higher-order gradient corrections to the kinetic energy and possibly also because of replacing μ by $\varepsilon_{\mathrm{HOMO}}$ (Hartree-Fock). These conclusions are unlikely to be affected even if wavefunctions of better quality are used.

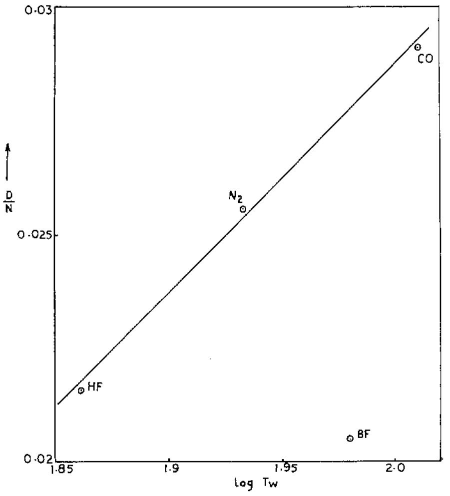

Fig. 4. Plot of D/N against $\log T_w$, in atomic units. The H_2 molecule is not shown

Table 1. Calculated electronic kinetic energy terms for five molecules in their ground states, using wavefunctions from Snyder and Basch [5]. D denotes dissociation energy. All values are in atomic units

Molecule	$\int \rho\, d\vec{r}$	T_0[a]	T_w	T_r	Double-zeta $\hat{T}$[b]	$T_0 + T_2$[c]	$T_0 + T_r$	D[d]
H_2	2.007	1.000	1.135	0.0788	1.128	1.126	1.079	0.1646
HF	10.003	91.43	72.61	8.234	100.01	99.50	99.66	0.2157
BF	14.000	130.97	95.55	0.2470	124.17	141.59	131.22	0.2867
N_2	13.958	101.45	85.62[e]	0.3184	108.74	110.96	101.76	0.3587
CO	14.012	126.66	102.67	3.498	112.65	138.07	130.16	0.4076

[a] $T_0 = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}\, d\vec{r}$

[b] Taken from [5]

[c] $T_2 = T_w/9$

[d] Taken from [7]

[e] Taking T_w for the N atom as 43.24, using Hartree-Fock atomic density [8], Yonei's [2] data for N_2 at R_{eq}, with $\lambda = 1$, correspond to $T_w(N_2, R_{eq}) = 85.38$

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References

1. Balàzs NL (1967) Phys Rev 156:42
2. Yonei K (1971) J Phys Soc Jpn 31:882
3. Wang WP, Parr RG (1977) Phys Rev A16:891
4. Mucci JF, March NH (1983) J Chem Phys 78:6187
5. Snyder LC, Basch H (1972) Molecular wavefunctions and properties. John Wiley, New York
6. Haq S, Chattaraj PK, Deb BM (1984) Chem Phys Lett 111:79
7. Huber K, Herzberg G (1979) Constants for diatomic molecules. Van Nostrand-Reinhold, New York
8. Clementi E, Roetti C, (1974) At Data Nucl Data Tables 14:177