ORIGINAL PAPER

# Scaling of some chemical properties of tetrahedral and octahedral molecules plus almost spherical C and B cages

**N. H. March · Á. Nagy**

**Abstract**    It is shown that for tetrahedral and octahedral molecules the quantity $aR_e/N^{1/3}$ is quadratic in the ratio $z/N$, where $R_e$ is the equilibrium bond length, $ze$ is the central charge and $N$ is the total number of electrons. Some scaling properties for the 'breathing' force constant $k$ are proposed for a series of 5 tetrachlorides.

In early work [1] by one of us, a simplistic self-consistent central field model using the Thomas-Fermi statistical method [1–3] was presented, motivated by the desire to study scaling properties of a variety of tetrahedral and octohedral (T and O) molecules. This prompted, much later, the study of Mucci and March [4] who proceeded, but now by semiempirical analysis, to relate the nuclear-nuclear potential energy at equilibrium, denoted throughout by $V_{nn}$, to the total number of electrons $N$ in the molecule. Their semiempirical result, which was, as is to be expected, subject to some relatively small scatter, reads

$$V_{nn} = aN^{5/3}, \tag{1}$$

where the contant $a$ is given by Mucci and March [4].

N. H. March
Department of Physics, University of Antwerp, Antwerp, Belgium

N. H. March
Oxford University, Oxford, UK

Á. Nagy (✉)
Department of Theoretical Physics, University of Debrecen, 4010 Debrecen, Hungary
e-mail: anagy@madget.atomki.hu

Returning to the model in [1], $V_{nn}$ was related exactly to the equilibrium bond length $R_e$ of a given T or O molecule by

$$V_{nn} = \frac{n(z + cn)e^2}{R_e}.$$ (2)

Here $ze$ is the central charge, while $ne$ is the total positive charge of all outer nuclei: for example for $SF_6$, $z = 16$ and $n = 54$, the total number of electrons $N$ in the neutral molecules treated throughout being evidently $z + n$. The constant $c$ in Eq. (2) is

$$c = \frac{3\sqrt{6}}{32} \approx 0.23$$ (3)

for tetrahedral and

$$c = \frac{1 + 4\sqrt{2}}{24} \approx 0.28$$ (4)

for octahedral molecules. To avoid the simplistic model [1]—see also March and Parr [5], let us next combine Eqs. (2) and (1) to reach the scaling prediction for the equilibrium bond length $R_e$ entering Eq. (2) as

$$\frac{aR_e}{N^{1/3}} = c + (1 - 2c)\frac{z}{N} + (c - 1)\left(\frac{z}{N}\right)^2.$$ (5)

To find the maximum values of $z/N$ for $aR_e/N^{1/3}$ for the two cases T and O, we differentiate Eq. (5) with respect to $z/N$ to find

$$\frac{\partial \frac{aR_e}{N^{1/3}}}{\partial \frac{z}{N}} = 1 - 2c + 2(c - 1)\frac{z}{N}.$$ (6)

$aR_e/N^{1/3}$ plotted in Fig. 1 shows a maximum at $z/N = (2c - 1)/2(c - 1)$. The maximum value of $aR_e/N^{1/3}$ is $1/(4(1 - c))$ ($\approx 0.31$ for tetrahedral and $\approx 0.35$ for octahedral molecules). Experimental $R_e$ data [6] for some tetrahedral molecules are shown in Fig. 2, and indeed there is only weak dependence on $z/N$ paralleling (Fig. 1).

We want to turn to relate next the 'breathing' force constant $k = \partial^2 E/\partial R^2|_{R_e}$ for T and O molecules to $R_e$. Turning back to the model [1], Bowers [7] fitted in this oversimplistic model when heavy atoms like Cl and Br are in the outer positions (in [1] Cl inner electrons were 'compressed' into nucleus), the scaling properies for the $R_e$ given by the Thomas-Fermi model in [1], namely
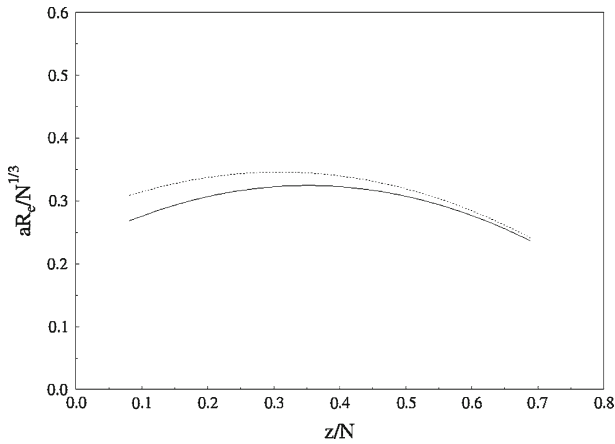
$$R_e = z^{-1/3}d\left(\frac{n}{z}\right),$$ (7)

**Fig. 1** The quantity $a R_e / N^{1/3}$ calculated from Eq. (5) for tetrahedral (*lower curve*) and octahedral (*upper curve*) molecules against $z/N$, where $R_e$ is the equilibrium bond length in Å, $ze$ is the central charge and $N$ is the total number of electrons
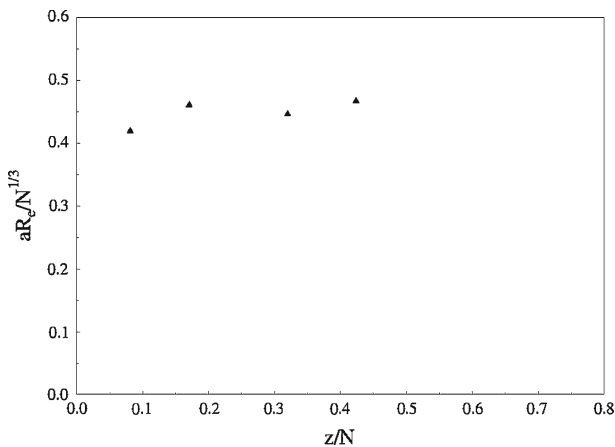


**Fig. 2** The quantity $R_e / N^{1/3}$ for tetrahedral molecules against $z/N$, where $R_e$ is the experimental equilibrium bond length in Å, $ze$ is the central charge and $N$ is the total number of electrons

where Bowers wrote the approximate form to fit the numerical results in [1] as

$$d = const \left( \frac{n}{z} \right)^{0.6}. \tag{8}$$

Similarly for $k$, in [7] a fit was made to predictions from [1], of the form

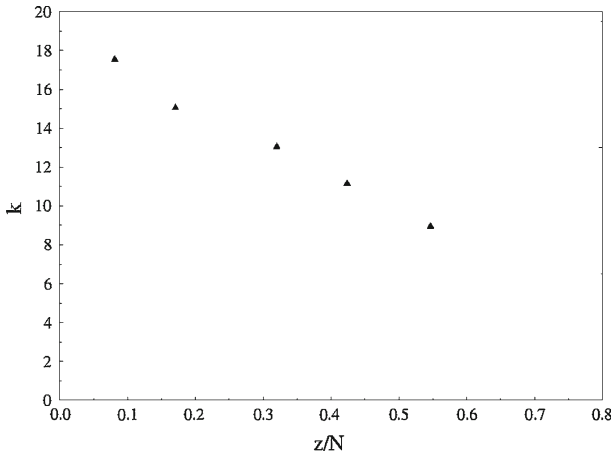$$k = z^3 g \left( \frac{n}{z} \right), \tag{9}$$

**Fig. 3** Experimental 'breathing' force constant $k$ (in $10^5$ dyne/cm) for 5 tetrachlorides versus $z/N$

where

$$g = const \left(\frac{n}{z}\right)^{-3.51}. \tag{10}$$

Raising $R_e$ in Eqs. (7) and (8) to the power 6 and multiplying the result by $k$

$$6 \ln R_e = \ln (z/k) + const \tag{11}$$

is too strong a dependence on $R_e$ to agree with experimental $\ln k$. Figure 3 therefore presents experimental data [6] for $k$ versus $z/n$ for some tetrahedral molecules.

Amovilli et al. [8] essentially replaced the use of TF statistical theory in [1] by the Hartree-Fock theory for the fullerenes $C_{50}$, $C_{60}$, $C_{70}$ and $C_{84}$ with 'almost spherical' C cages.

Denoting by $n$ the number of C atoms, we summarize essentially their numerical values for the above 4 cages in Table 1. The energy $E(n, R)$ is shown in [8] to be well represented by

$$\frac{E(n, R)}{n} = a_c + \frac{b_c n^{1/2}}{R} + \frac{c_c n}{R^2}. \tag{12}$$

The values of the constants $a_c$, $b_c$ and $c_c$ can be found in [8]. The 'law' $R_e$ proportional to $n^{1/2}$ is essentially, a statement of constant surface area on the fullerene spheres per C atom, as stressed for example in [8].

Following the discussion earlier on T and O molecules, let us briefly consider for the case of the C cages the breathing force constant $k = d^2E/dR^2|_{R_e}$. Using Eq. (12) we readily find

$$\frac{1}{n}\frac{dE}{dR} = -\frac{b_c n^{1/2}}{R^2} - \frac{2c_c n}{R^3} \tag{13}$$

**Table 1** Ground-state energies per atom and equilibrium radii $R_e$ in Å from [8] for almost spherical C cages

| $n$ | 50 | 60 | 70 | 84 |
|---|---|---|---|---|
| $E/n$ | −37.59 | −37.60 | −37.59 | −37.59 |
| $R_e$ | 3.278 | 3.582 | 3.865 | 4.256 |
| $R_e/\sqrt{n}$ | 0.463 | 0.462 | 0.462 | 0.464 |

and the equilibrium radius $R_e$ is evidently given by setting $dE/dR = 0$ to find

$$R_e = -\frac{2c_c n^{1/2}}{b_c}. \tag{14}$$

Finally, from Eq. (13) we readily obtain

$$\frac{1}{n}\frac{d^2 E}{dR^2} = \frac{2b_c n^{1/2}}{R^3} + \frac{6c_c n}{R^4} \tag{15}$$

and hence the breathing force contant $k$ is given by

$$k = \left.\frac{d^2 E}{dR^2}\right|_{R=R_e} = \frac{2b_c n^{3/2}}{R^3} + \frac{6c_c n^2}{R^4}. \tag{16}$$

To relate $k$ and $R_e$, as we did above for the T and O molecules, let us use Eq. (14) in Eq. (16) to find

$$k = \frac{b_c^4}{8c_c^3}. \tag{17}$$

So, the breathing force constant is predicted from the Hartree-Fock model of the $\pi$-electrons (of course 1 per C atom) to be independent of $R_e$ and given by the known constants $b_c$ and $c_c$ entering the energy equation (12).

Before summarizing, it is relevant to make a brief digression to relate to the lower dimensionality example of planar ring clusters. The work of Amovilli and March [9] is, essentially, the two-dimensional analogue of the Thomas-Fermi (TF) self-consistent field treatment of [1].

Briefly then, the chemical potential $\mu$, the same at every point in such a 2D cluster, is in the TF method given by

$$\mu = \frac{p_F^2(\mathbf{r})}{2m} + V(\mathbf{r}), \tag{18}$$

where $p_F(\mathbf{r})$ is the maximum momentum at position $\mathbf{r}$ in this semiclassical treatment, while $V(\mathbf{r})$ is the self-consistent electrostatic potential. To complete the TF method in the present example, the customary phase space arguments for 2D yield the ground-state density $n(\mathbf{r})$ as
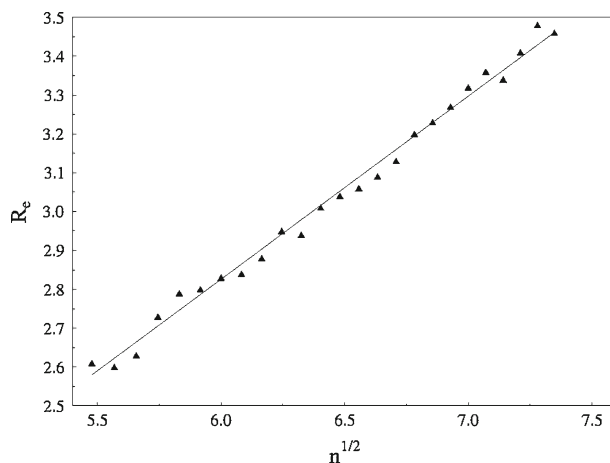
**Fig. 4** Equilibrium radius (in Å) of the spheroidal boron cages against $n^{1/2}$, where $n$ is the number of boron atoms. *Triangles* refer to ab initio computed values

$$n(\mathbf{r}) = \frac{2\pi p_F^2(\mathbf{r})}{h^2}. \tag{19}$$

Then to relate $n$ and $V$ we have the 2D Poisson equation, now in linear form when Eqs. (18) and (19) are employed:

$$\frac{d^2 V(r)}{dr^2} + \frac{1}{r}\frac{dV(r)}{dr} = 4V(r). \tag{20}$$

This self-consistent equation (20) being linear in contrast to the 3D non-linear form in [1], can be solved analytically in terms of Bessel functions.

Amovilli and March, following [1] made comparison with known results for H and C planar ring clusters. Interesting semiquantitative agreement was found, from such a crude model, particularly for the H clusters.

Amovilli and March [10] extended the simple model in [1] to boron cages using Hartree-Fock calculations. These authors found that the equilibrium radius of the spheriodal boron cages is proportional to the squareroot of $n$, the number of boron atoms in the cluster. We have redrawn the result of [10] therefore in Fig. 4, to make the above comment concrete.

In summary, the key result for T and O classes of molecules is Eq. (5). This shows that the quantity $aR_e/N^{1/3}$ is quadratic in the ratio $z/N$, where $ze$ is the central charge and $N$ is the total number of electrons. As $z/N$ tends to zero, this ratio tends to the constant $c$, which is $\approx 0.23$ and $0.27$ for T and O molecules, respectively (see Eqs. (3) and (4) for exact values of $c$). There is a maximum which occurs near $z/N = 1/3$. The maximum value of $aR_e/N^{1/3}$ is $1/(4(1-c))$. Then some scaling properties for the 'breathing force constant $k$ are proposed for a series of 5 tetrachlorides, $k$ correlating well with a low-order polynomial in $z/N$.

Attention is then shifted to 'almost' spherical C and B cages. As shown for C cages $C_{50}$, $C_{60}$, $C_{70}$ and $C_{84}$ by Amovilli et al. [8], $R_e$ is proportional $n^{1/2}$, where $n$ is the number of C atoms. Our arguments here suggest that the force constant $k$ is either independent of, or very insensitive to, the value of $n$. For B cages, as Amovilli and March [10] demonstrate, $R_e = 0.471 n^{1/2}$Å having the same $n$ dependence as for the four C cages discussed above.

Finally, planar ring clusters are briefly referred to, again in relation to scaling properties.

# References

1. N.H. March, Proc. Cambridge Philos. Soc. **48**, 665 (1952)
2. L.H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1926)
3. E. Fermi, Z. Phys. **48**, 73 (1928)
4. J.F. Mucci, N.H. March, J. Chem. Phys. **82**, 5099 (1985)
5. N.H. March, R.G. Parr, Proc. Natl. Acad. Sci. USA **77**, 6285 (1980)
6. G. Herzberg, *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules* (van Nostrand, New York, 1950)
7. W.A. Bowers, J. Chem. Phys. **21**, 117 (1953)
8. C. Amovilli, I.A. Howard, D.J. Klein, N.H. March, Phys. Rev. A **66**, 013210 (2002)
9. C. Amovilli, N.H. March, Phys. Rev. A **73**, 063205 (2006)
10. C. Amovilli, N.H. March, Chem. Phys. Lett. A **347**, 459 (2001)