Finer examination of Politzer's improved approximate energy formula for molecules

Tosinobu Anno

Articles you may be interested in

Energy formulas for atoms and molecules
J. Chem. Phys. **80**, 5070 (1984); 10.1063/1.446575

An improved approximate energy formula for molecules in terms of corrected free atom energies
J. Chem. Phys. **78**, 4782 (1983); 10.1063/1.445281

Systematic study of Politzer's energy relation for atoms
J. Chem. Phys. **72**, 6044 (1980); 10.1063/1.439060

An improved approximate energy formula for molecules
J. Chem. Phys. **70**, 1067 (1979); 10.1063/1.437526

The Politzer and the Ruedenberg type energy relations for molecules in their nonequilibrium configurations
J. Chem. Phys. **69**, 5213 (1978); 10.1063/1.436476

Finer examination of Politzer's improved approximate energy formula for molecules

Tosinobu Anno

Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Fukuoka, 810 Japan

In a recent note, Politzer[1] has shown that his relation[2] connecting the total energy E of a molecule with the total electrostatic potential $V_{0,A}$ at the nucleus of A having nuclear charge Z_A within the molecule, $E = (\frac{3}{7}) \times \sum_A Z_A V_{0,A}$, can be improved considerably, if it is mod-

ified to

$$E = \sum_A k_A Z_A V_{0,A} , \qquad (1)$$

by replacing the factor $\frac{3}{7}$ by a parameter k_A which would

TABLE I. Comparison of molecular energies calculated by various approximate methods.[a]

Molecule[b]	E_{HF}	E	$E - E_{HF}$	$\sum_A E_A^{atom}$	$\sum_A E_A^{atom} - E_{HF}$	$E^{modified}$	$E^{modified} - E_{HF}$
BF[c]	−124.1659	−123.8636	0.3023	−123.9384	0.2275	−124.0646	0.1013
CO[c]	−112.7860	−112.3561	0.4299	−112.4980	0.2880	−112.7421	0.0439
HF[d]	−100.0705	−100.1393	−0.0688	−99.9093	0.1612	−100.3075	−0.2370
HCl[d]	−460.1119	−460.1925	−0.0806	−459.9818	0.1301	−460.3763	−0.2644
H$_2$[e]	−1.1336	−1.1024	0.0312	−1.0000	0.1336	(−1.1336)	(0.0)
B$_2$[e]	−49.0909	−48.9979	0.0930	−49.0581	0.0328	(−49.0909)	(0.0)
C$_2$[e]	−75.4062	−75.1719	0.2343	−75.3772	0.0290	(−75.4062)	(0.0)
N$_2$[e]	−108.9928	−108.4229	0.5629	−108.8018	0.1910	(−108.9928)	(0.0)
O$_2$[e]	−149.6659	−149.1297	0.5362	−149.6187	0.0472	(−149.6659)	(0.0)
F$_2$[e]	−198.7701	−198.4615	0.3086	−198.8186	−0.0485	(−198.7701)	(0.0)
P$_2$[f]	−681.5004	−681.5141	−0.0137	−681.4374	0.0630	(−681.5004)	(0.0)
S$_2$[g]	−795.0397	−794.6478	0.3919	−795.0094	0.0303	(−795.0397)	(0.0)
Cl$_2$[h]	−918.9871	−918.6466	0.3405	−918.9636	0.0235	(−918.9871)	(0.0)
H$_2$O[i]	−76.0649	−76.0858	−0.0209	−75.8094	0.2555	−76.3557	−0.2908
NO$_2$[j]	−204.0679	−202.9746	1.0933	−204.0197	0.0482	−203.7899	0.2780
SO$_2$[k]	−546.831	−546.3745	0.4565	−547.1236	−0.2926	−547.0968	−0.2658
O$_3$[j]	−224.3093	−223.2243	1.0850	−224.4281	−0.1188	−224.0270	0.2823
H$_2$S[l]	−398.6862	−398.6789	0.0073	−398.5049	0.1813	−398.8920	−0.2058
PH$_3$[l]	−342.4603	−342.3998	0.0605	−342.2187	0.2416	−342.4382	0.0221
SiH$_4$[l]	−291.2355	−291.1790	0.0565	−290.8543	0.3812	⋯	⋯
H$_2$CO[m]	−113.8917	−113.5781	0.3136	−113.4980	0.3937	−113.9646	−0.0729

[a]All energies are given in hartrees. Column headings stand for molecular energies, or the differences thereof, calculated with the following methods; E_{HF} near Hartree–Fock method; E with Eq. (1) with k_A appropriate to the free atoms; $\sum_A E_A^{atom}$ sum of the Hartree–Fock energies of the ground-state atoms involved in the molecule; $E^{modified}$ with Eq. (2) with k_A^{mol} obtained from the data of homonuclear diatomic molecule A$_2$ (see text).

[b]All molecules treated here are those in their ground states. Reference attached to each of the molecules is referred to the source from which E_{HF} and $V_{0,A}$ [see Eqs. (1) and (2)] are taken. If the data based on several basis sets are given in the source, short comments are given in the respective reference to indicate which set of the data is adopted in the present work.

[c]W. M. Huo, J. Chem. Phys. **43**, 624 (1964). "Experimental R_e, atomic built up set".

[d]A. D. McLean and M. Yoshimine, J. Chem. Phys. **47**, 3256 (1967). "Cade–Huo augmented" for HF and "$BA + P$" for HCl.

[e]P. E. Cade and A. C. Wahl, Atomic Data and Nuclear Data Tables **13**, 339 (1974).

[f]R. S. Mulliken and B. Liu, J. Am. Chem. Soc. **93**, 6738 (1971).

[g]F. D. Wayne and E. A. Colbourn, Mol. Phys. **34**, 1141 (1977); F. D. Wayne (private communications).

[h]T. L. Gilbert and A. C. Wahl, J. Chem. Phys. **55**, 5247 (1971). For $R = 3.8$ a.u. which is essentially close to the calculated equilibrium distance 3.756 a.u. Detailed data necessary for calculating molecular k_A value are compiled in M. Krauss, *Compendium of ab initio Calculations of Molecular Energies and Properties* (Technical Note 438, Natl. Bur. Stnds., Washington, D.C., 1967), p. 114.

[i]B. Rosenberg, W. C. Ermler, and I. Shavitt, J. Chem. Phys. **65**, 4072 (1976). Point No. 9, which is the nearest to the potential minimum.

[j]S. Rothenberg and H. F. Schaefer, III, Mol. Phys. **21**, 317 (1971). "With d functions".

[k]B. Roos and P. Siegbahn, Theoret. Chim. Acta **21**, 368 (1971). "$3d$ on S and O".

[l]S. Rothenberg, R. H. Young, and H. F. Schaefer, III, J. Am. Chem. Soc. **92**, 3243 (1970).

[m]D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. **50**, 2216 (1969).

be a specific property of each atom A. It is true that the improvement is considerable but the agreement of E from Eq. (1) with E_{HF} [E value obtained with the near Hartree–Fock (HF) calculation of the molecule] seems to be still inadequate for us to be able to talk about quantities of chemical interest, so far as k_A is chosen according to the original prescription.[1] In the present paper, it will be shown that subtle change of k_A due to the change of the nuclear environment is to be taken into account in order that one can obtain E with Eq. (1) accurately enough.

In Table I, E_{HF} and E obtained with Eq. (1) by using the k_A value for the free neutral atom given in Politzer[1] are listed for various molecules, including most of the molecules treated by Politzer.[1] In the same table, $\sum_A E_A^{atom}$, the sum of the HF energies of the ground-state atoms[3] involved in the molecule, is also given. An important point to be noted is the fact that $E - E_{HF}$, which represents the error of E, is *larger* than $\sum_A E_A^{atom} - E_{HF}$ for most of the molecules except those containing only one atom other than hydrogen. This means that Eq. (1) is still inadequate to predict E in such an accuracy that is enough for us to be able to discuss heat of atomization of these molecules if it is used as was originally prescribed.[1] It is expected that k_A appropriate for atom A within a molecule might be different from such a value that is appropriate for the free atom and that Eq. (1) might be improved if it is modified as

$$E^{modified} = \sum_A k_A^{mol} Z_A V_{0,A} , \qquad (2)$$

by using k_A^{mol}, the k_A value appropriate to the atom A within the molecule. If one assumes transferability of k_A^{mol} among various molecules, k_A^{mol} is most conveniently determined from the HF data on the A_2 molecule, using Eq. (2) in such a way that $E^{modified}$ agrees with E_{HF}, since k_A^{mol} then is the only parameter to be determined. The k_A values thus determined are given in Table II and are compared with those for the free atoms as well as with those for the singly negative and the single positive ions. We are now in a position to calculate molecular energies with Eq. (2). The results are also given in Table I. It may be seen that $E^{modified} - E_{HF}$ is considerably smaller than $E - E_{HF}$ except for the HF, HCl, H_2O, and the H_2S molecule. It is not claimed that $E^{modified}$ is close enough to E_{HF} for us to be able to talk about heat of atomization by using $E^{modified}$ in place of E_{HF} but $E^{modified}$ is certainly closer to E_{HF} than E, with a few exceptions mentioned above. This means that changes not only of

TABLE II. k_A values in various nuclear environments.

A	+1 ion	Neutral atom[a]	−1 ion	A_2 molecule[b]
H		0.500 00	⋯	0.514 33
B	0.443 97	0.431 11	0.421 50	0.431 93
C	0.439 42	0.427 62	0.418 18	0.428 97
N	0.434 76	0.423 85	0.414 84	0.426 05
O	0.430 29	0.420 10	0.411 59	0.421 61
F	0.425 90	0.416 52	0.408 48	0.417 17
Si	0.421 64	0.419 00	0.416 87	⋯
P	0.422 20	0.419 50	0.417 36	0.419 54
S	0.422 48	0.419 80	0.417 54	0.420 01
Cl	0.422 57	0.419 87	0.417 52	0.420 03

[a]It is to be noted that k_A value listed in Politzer[1] for the neutral C, Si, P, and S are 0.427 64, 0.419 01, 0.419 55, and 0.419 81, respectively, because he has used the numerical Hartree–Fock (HF) data [C. Froese Fischer, Atomic Data and Nuclear Data Tables 4, 301 (1972); *ibid*. 12, 87 (1973); J. B. Mann, Atomic Data and Nuclear Data Tables 12, 1 (1973)] rather than the analytical HF data of Clementi.[3] No difference exists for the other neutral atoms listed in this Table. In calculating E in Table I, Politzer's k_A values are adopted to facilitate a comparison with Politzer's E.
[b]As for the source on the HF data of the A_2 molecules from which k_A^{mol} are calculated, see footnotes to Table I.

$V_{0,A}$ but also of k_A, when atoms get into a molecule, ought to be taken into account if the molecular energy is to be calculated with a formula of the type of Eq. (1) with an accuracy sufficient enough to have chemical significance.

[1]P. Politzer, J. Chem. Phys. 70, 1067 (1979).
[2]P. Politzer, J. Chem. Phys. 64, 4239 (1976). Politzer's relation was originally written as $E = (\frac{3}{7})(V_{Ne} + 2V_{NN})$, by using the nuclear–electronic (V_{Ne}) and the nuclear–nuclear interaction potential (V_{NN}), but it can easily be shown that this relation can also be written as $E = (\frac{3}{7})\sum_A Z_A V_{0,A}$.
[3]E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables 14, 177 (1974).