REGULAR ARTICLE

Electrostatic potentials at the nuclei of atoms and molecules

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Abstract

The electrostatic potential at the nucleus of an atom, whether in the free state or in a molecule, is qualitatively a characteristic property of the atom. It changes remarkably little from one molecular environment to another. The energies of atoms and molecules can be expressed both rigorously and approximately in terms of the electrostatic potentials at their nuclei. Molecular energies can be written entirely as summations over atomic contributions, with no explicit interatomic terms. This provides a basis for estimating the energy of an atom in a molecule. Overall, the present study supports the validity of the atoms-in-molecules concept.

Keywords Electrostatic potentials at nuclei · Atoms in molecules · Atomic energies · Molecular energies

1 The ambiguous nature of the chemical bond

In 1992, taking care to avoid understatement, Pauling expressed his view that "The concept of the chemical bond is the most valuable concept in chemistry. Its development over the past 150 years has been one of the greatest triumphs of the human intellect." [1] However, just 15 years later, in a special issue of the Journal of Computational Chemistry entitled "90 Years of Chemical Bonding," Frenking and Shaik commented that "we are still far from understanding the nature of the chemical bond" [2], which was echoed by Jacobsen, "many questions remain open in the quest for a unified and complete understanding of the true nature of the chemical bond" [3].

But is such a quest even meaningful? Jacobsen goes on to say that "it has become clear that the chemical bond per se does not exist. Each bond possesses its very own specific character," [3]. Foroutan-Nejad et al. seem to share this view: "there is no general theoretical Scheme that may claim to encompass the description of all known types of chemical bonds." [4]. Gillespie and Robinson go further: "a bond has no physical reality." [5] Bader, as always is emphatic:

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"a 'bond' is neither measurable nor susceptible to theoretical definition." [6] Instead of bonds, he speaks of "bonded interactions."

Questioning the very concept of a chemical bond is not a recent development. Just a year after Pauling's famous treatise [7], The Nature of the Chemical Bond, Allen and Shull noted that it is "extremely difficult to see factors significant in stabilizing a particular configuration of electrons and nuclei" [8].

This brings up a yet more fundamental issue of contention. Chemical bonds are typically viewed as linking atoms in molecules. But is it even meaningful to speak of atoms in molecules? Quantum chemistry views a molecule as a collection of electrons and nuclei. As Ivanic et al. pointed out, "the resolution of molecules in terms of atoms is not *fundamental* to rigorous physical theory." [9] Parr et al. noted that the atoms-in-molecules concept is ambiguous and arbitrary [10], and Gilbert et al. put it succinctly, "There exists no quantum mechanical definition of an atom within a molecule and, therefore, any attempt to extract atomic identity is arbitrary." [11]

Bader, developer of the Quantum Theory of Atoms in Molecules (QTAIM) [12, 13] naturally strongly disagrees [14]. However, while QTAIM is mathematically elegant, its relevance to chemical realities is increasingly being questioned [4, 15–29].

Can one aspire to explain the nature of bonds between atoms in molecules if it is not even established that there are indeed atoms in molecules? This dilemma has not prevented a variety of explanations of chemical bonding from

being put forth: resonance, electronic charge buildup in internuclear regions, kinetic energy lowering, orbital interference, charge transfer, etc. Carbó-Dorca commented that "It might be almost impossible to describe in a short account the different manners by which the chemical bond has been described" [30].

In this brief overview, we have sought to demonstrate some fundamental disagreements that prevail in the area of chemical bonding. Our present objective is not to try to resolve any issues, but simply to provide some additional perspective.

2 Electrostatic potentials at nuclei of atoms and molecules

The electrostatic potential $V_{0,A}$ that is created at any nucleus A of a molecule by its electrons and the other nuclei is given rigorously, following Coulomb's Law, by Eq. (1):

$$V_{0,A} = \sum_{B \neq A} \frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r})d\mathbf{r}}{|\mathbf{r} - \mathbf{R}_A|} \tag{1}$$

$\mathbf{R}_A$ is the position of nucleus A, having charge Z_A, and $\mathbf{R}_B$ and Z_B are the position and charge of any other nucleus B; $\rho(\mathbf{r})$ is the molecule's electronic density. The two terms in Eq. (1) represent, respectively, the positive contribution of the other nuclei and the negative one of the electrons.

If A is the nucleus of just a single free atom, then the summation over other nuclei does not appear. The electrostatic potential V_0 at the nucleus of a free atom is,

$$V_0 = - \int \frac{\rho(\mathbf{r})d\mathbf{r}}{\mathbf{r}} \tag{2}$$

Now $\rho(\mathbf{r})$ is the electronic density of the atom, and $\mathbf{r}$ is relative to its nucleus.

An important feature of the electrostatic potential is that it is a real physical property, an observable. It can be determined experimentally, by diffraction methods [31–33], as well as computationally.

It has been pointed out in the past that the electrostatic potential at the nucleus of a given atom is relatively insensitive to the atom's molecular environment [34, 35]. We will now investigate this more extensively and in greater detail.

In Table 1 are the computed electrostatic potentials at the nuclei of the indicated atoms in a variety of molecules as well as in the free atoms. The calculations were carried out at the B3P86/6–311 + G(3df,2p) level, using Gaussian 09 [36].

The most striking feature of Table 1 is how little the electrostatic potential at an atom's nucleus changes even in quite different environments, not only neutral molecules but ions as well. For example, the $V_{0,A}$ of the nitrogen atoms

in Table 1 are all within 1.7% of the free atom value; this includes the nitrogen in the N_3^- and NO_3^- anions, in a series of neutral molecules of differing polarities, and in the NH_4^+ cation. For the chlorine atoms, the $V_{0,A}$ are within 0.6% of the free atom V_0 in a series that includes the Cl^- anion, the highly polar LiCl and several neutral covalent molecules, among them being Cl_2.

This relative insensitivity to environment is particularly noteworthy because the two contributions to $V_{0,A}$, the nuclear and the electronic, can change very considerably from one molecule to another. Consider, for instance, the carbon atoms in $H_2C=O$ and $(H_2N)_2C=O$. The nuclear and electronic contributions to the electrostatic potentials at the carbon nuclei are quite different in the two molecules: + 4.496 and – 19.179 hartrees in $H_2C=O$ and + 9.916 and – 24.567 hartrees in $(H_2N)_2C=O$. Yet the net potentials at the carbon nuclei are nearly the same in both molecules, − 14.683 and − 14.651 hartrees, respectively (Table 1).

As another example, take the phosphorus in PF_3 and $Cl_3P=O$. The nuclear and electronic contributions to the potentials at the phosphorus nuclei in these molecules differ considerably: + 9.065 and − 63.101 hartrees in the former and + 16.414 and − 70.422 hartrees in the latter. However, the resulting net potentials at the phosphorus nuclei are very similar,− 54.036 and − 54.007 hartrees.

Table 1 and these examples can be interpreted as indicating that the electrostatic potential at the nucleus of an atom A in a molecule reflects almost entirely its own electronic density; the contributions of the other electrons and nuclei largely cancel. The electronic density of the atom undergoes some degree of polarization in forming the molecule and this has a minor effect upon its $V_{0,A}$, which becomes more (less) negative as electronic charge is polarized toward (away from) the nucleus of A. $V_{0,A}$ is most negative when the atom A is part of an anion, least negative when part of a cation (Table 1). However, $V_{0,A}$ is in all cases very characteristic of the atom A, as can be seen in Table 1 and in the excellent correlation of the free atom V_0 with their nuclear charges, Fig. 1.

Hydrogen is an exception to the generalization that $V_{0,A}$ values are relatively insensitive to molecular environment; its $V_{0,H}$ sometimes differs very considerably from that of the free atom, as shown in Table 2. This can be understood by recognizing that hydrogen has no inner electrons that can provide the basis for a relatively stable $V_{0,H}$; its only electron is involved in bonding. The absence of inner electrons makes both the hydrogen atom and the hydrogen molecule atypical, as has been pointed out a number of times [29, 37–40]. (It is ironical that H_2 has traditionally been used as the model for the covalent bond.)

It is tempting to try to rationalize the $V_{0,A}$ values in Table 1 in terms of electronegativities. On that basis, the electrostatic potential at the nucleus of an atom would be

Table 1 Computed electrostatic potentials at nuclei of indicated atoms

Atom	Molecule or free atom	$V_{0,A}$ (hartrees)	Atom	Molecule or free atom	$V_{0,A}$ (hartrees)
Li	Li_2	− 5.746	N	N_3^- (end N's)	− 18.645
	LiF	− 5.743		N_3^- (central N)	− 18.502
	LiH	− 5.740		NH_3	− 18.421
	Free atom	− 5.719		H_2P–CN	− 18.403
	LiCl	− 5.701		$(H_2N)_2C{=}O$	− 18.373
Be	Free atom	− 8.421		NH	− 18.364
	BeH	− 8.413		NO_3^-	− 18.352
B	BH	− 11.398		Pyrrole	− 18.346
	Free atom	− 11.394		Free atom	− 18.344
	B_2	− 11.385		N_2	− 18.320
	BF	− 11.381		$ClH_2SiON(CH_3)_2$	− 18.314
C	Pyrrole (C_β)	− 14.796		HNO	− 18.284
	Furan (C_β)	− 14.777		NO_2	− 18.158
	Pyrrole (C_α)	− 14.760		NH_4^+	− 18.023
	$(H_3C)_2S{=}O$	− 14.751	O	OH^-	− 22.737
	H_2P–CN	− 14.743		NO_3^-	− 22.579
	Furan (C_α)	− 14.729		$(H_3C)_2S{=}O$	− 22.414
	CH	− 14.712		$(H_2N)_2C{=}O$	− 22.410
	Free atom	− 14.703		$Cl_3P{=}O$	− 22.364
	C_2	− 14.700		H_2O	− 22.361
	$H_2C{=}O$	− 14.683		$H_2C{=}O$	− 22.349
	$(H_2N)_2C{=}O$	− 14.651		OH	− 22.313
	CCl_4	− 14.527		SO_2	− 22.312
	CF_4	− 14.417		Furan	− 22.294
				CO_2	− 22.286
				CO	− 22.268
				Free atom	− 22.266
				NO_2	− 22.261
				O_2	− 22.230
				F_2O	− 22.159
				H_3O^+	− 21.923
F	LiF	− 26.765	P	P_2	− 54.177
	HF	− 26.599		PH	− 54.174
	PF_3	− 26.555		Free atom	− 54.165
	CF_4	− 26.528		H_2P–CN	− 54.142
	Free atom	− 26.520		PF_3	− 54.036
	F_2O	− 26.513		$Cl_3P{=}O$	− 54.007
	BF	− 26.511			
	F_2	− 26.494	S	SH	− 59.220
				Thiophene	− 59.219
Na	Na_2	− 35.445		S_2	− 59.200
	NaH	− 35.435		Free atom	− 59.200
	Free atom	− 35.430		$(H_3C)_2S{=}O$	− 59.152
	Na^+	− 35.135		SO_2	− 59.069

Table 1 (continued)

Mg	Free atom	− 39.928	Cl	Cl⁻	− 64.730
	MgH	− 39.906		LiCl	− 64.506
	Mg⁺²	− 39.153		ClH₂SiON(CH₃)₂	− 64.427
				HCl	− 64.395
Al	AlH	− 44.526		SiCl₄	− 64.380
	Free atom	− 44.517		CCl₄	− 64.370
	Al₂	− 44.513		Free atom	− 64.359
				Cl₃P=O	− 64.358
Si	Si₂	− 49.270		Cl₂	− 64.349
	SiH	− 49.267		ClO	− 64.312
	Free atom	− 49.261			
	ClH₂SiON(CH₃)₂	− 49.248			
	SiCl₄	− 49.146			

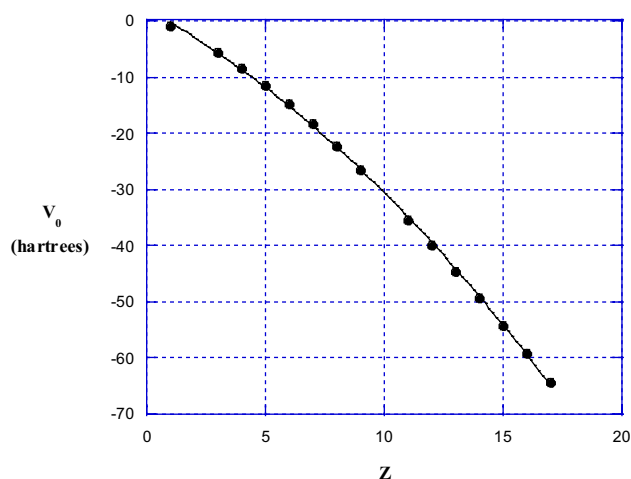Computational level: B3P86/6–311 + G(3df,2p)

Fig. 1 Relationship between computed electrostatic potential at nucleus of free atom and nuclear charge, for atoms in Table 1 plus hydrogen atom. $R^2 = 0.9996$

Table 2 Computed electrostatic potentials at nuclei of hydrogen atoms

Molecule or free atom	$V_{0,H}$ (hartrees)
OH⁻	− 1.366
LiH	− 1.237
NaH	− 1.215
AlH	− 1.175
MgH	− 1.164
SiH	− 1.121
ClH₂SiON(CH₃)₂ (H on Si)	− 1.121
Pyrrole (H$_\beta$)	− 1.114
H₂	− 1.108
Furan (H$_\beta$)	− 1.092
Pyrrole (H$_\alpha$)	− 1.092
Furan (H$_\alpha$)	− 1.081
H₂C=O	− 1.080
PH	− 1.069
NH₃	− 1.064
H₂P–CN	− 1.035
NH	− 1.028
H₂O	− 1.000
OH	− 0.971
Free atom	− 0.995
HCl	− 0.949
HF	− 0.920
NH₄⁺	− 0.701
H₃O⁺	− 0.595

Computational level: B3P86/6–311 + G(3df,2p)

less (more) negative as the remainder of the molecule is more (less) electron attracting. In some instances, this does account for the observed $V_{0,A}$. Thus, the carbon in CF_4 has a less negative $V_{0,C}$ than does the carbon in CCl_4. The nitrogen in pyrrole has a more negative $V_{0,N}$ than the one in NO_2.

However, electronegativity does not explain all of the trends and patterns in Table 1. For example, why are the $V_{0,A}$ of many of the homonuclear diatomics less negative than for the free atoms? Why is it that in F_2O, which combines the two most electronegative atoms, *both* $V_{0,F}$ and $V_{0,O}$ are less negative than for the free atoms? The lithium in LiF, LiH and LiCl is expected to be positive in character, yet in both LiF and LiH the potential at the lithium nucleus is more negative than in the free lithium atom.

3 Atomic and molecular energies from electrostatic potentials at nuclei

In 1962, Wilson used the Hellman–Feynman theorem [41, 42] to derive an *exact* formula for the energy of a molecule in terms of its electronic density [43]. This was two years prior to the Hohenberg–Kohn theorem [44], which established the electronic density as the fundamental determinant of all molecular properties.

It has subsequently been demonstrated that Wilson's result can be re-formulated to give the energy of an N-electron molecule rigorously as a function of the electrostatic potentials at its nuclei [45, 46]:

$$E_{mol} = \sum_A z_A \int_{\lambda=0}^{1} \left[V_{0,A}(\lambda) \right]_N d\lambda \tag{3}$$

In Eq. (3), λ is a scaling parameter such that the charge on any nucleus Z_i is λz_i, where λ can vary between zero and one. In the actual molecule, $\lambda = 1$ and $z_i = Z_i$ for each nucleus. The effect of λ is to make all of the nuclear charges increase in a concerted manner from zero to their true values.

The atomic version of Eq. (3) had already been introduced by Foldy [47] some years before Wilson's work:

$$E_{atom} = \int_{Z'=0}^{Z} \left[V_0(Z') \right]_N dZ' \tag{4}$$

The actual application of eqs. (3) and (4) is challenging; e.g., the integrals are to be evaluated holding the numbers of electrons constant. Conceptually, however, these equations are quite significant. They show that the energy of an atom or molecule, which is a two-electron property, can be expressed *rigorously* in terms of the electrostatic potentials at the nuclei; these are one-electron properties but they evidently take account of electron–electron repulsion. This is a direct manifestation of the Hohenberg–Kohn theorem.

Furthermore, the molecular energy formula, Eq. (3), is simply the atomic formula, Eq. (4), summed over all of the constituent atoms. There are no explicit interaction or "mixing" terms. This is certainly consistent with the concept of atoms in molecules.

The difficulty of actually applying eqs. (3) and (4) has stimulated the development of a variety of approximate relationships between energies and electrostatic potentials at nuclei. There have been several reviews of this work [34, 35, 48–53].

An interesting aspect of this arises from the fact that approximate solutions of the Schrödinger equation often give V_0 and $V_{0,A}$ more accurately than the total energies. For instance, Hartree–Fock atomic and molecular energies are correct through first-order but Hartree–Fock electrostatic potentials at nuclei are correct through second-order [49, 50, 54]. This means that Hartree–Fock V_0 or $V_{0,A}$ inserted into an appropriate approximate E–V_0 or E–$V_{0,A}$ relationship can produce energies that are better than Hartree–Fock, i.e., contain significant amounts of correlation energy. This has been demonstrated [49, 50, 55].

4 Energies of atoms in molecules

Equation (4) suggests an approximate proportionality between E_{atom} and ZV_0, and Eq. (3) similarly suggests one between E_{mol} and $\sum_A Z_A V_{0,A}$. We have investigated these possibilities, using the computed data in Tables 1 and 2 and the exact atomic and molecular energies in Tables 3 and 4.

Figures 2 and 3 show that there are indeed excellent correlations between the exact E_{atom} and ZV_0 for the atoms in Table 3 and between the exact E_{mol} and $\sum_A Z_A V_{0,A}$ for the molecules in Table 4. R^2 is 1.000 in both cases. Equations (5) and (6) describe these relationships.

$$E_{atom} = 0.4196(ZV_0) - 0.1531 \tag{5}$$

$$E_{mol} = 0.4199 \left(\sum_A Z_A V_{0,A} \right) - 1.050 \tag{6}$$

Note that the slopes of the lines are essentially the same, and they both go nearly through the origins.

Equation (5) is almost identical with an atomic energy formula that comes out of Thomas–Fermi theory [56,

Table 3 Properties of free atoms

Atom	ZV_0(hartrees)[a]	E_{atom}(exact, hartrees)[b]
Li	− 17.157	− 7.478
Be	− 33.684	− 14.667
B	− 56.970	− 24.654
C	− 88.218	− 37.845
N	− 128.408	− 54.589
O	− 178.128	− 75.068
F	− 238.680	− 99.734
Na	− 389.730	− 162.255
Mg	− 479.136	− 200.053
Al	− 578.721	− 242.346
Si	− 689.654	− 289.359
P	− 812.475	− 341.259
S	− 947.200	− 398.110
Cl	− 1094.103	− 460.148

[a]The V_0 values are from Table 1
[b]Reference [56]

Table 4 Properties of molecules

Molecule	$\sum_A Z_A V_{0,A}$ (hartrees)[a]	E_{mol}(exact, hartrees)[b]
NH_3	− 132.139	− 56.564
C_2	− 176.400	− 75.923
H_2O	− 180.888	− 76.440
HF	− 240.311	− 100.460
N_2	− 256.480	− 109.542
CO	− 266.308	− 113.327
$H_2C=O$	− 269.050	− 114.510
HNO	− 307.287	− 130.485
O_2	− 355.680	− 150.328
CO_2	− 444.170	− 188.603
F_2	− 476.892	− 199.530
HCl	− 1095.664	− 460.818
ClO	− 1271.624	− 535.320
P_2	− 1625.310	− 682.703
S_2	− 1894.400	− 796.383
Cl_2	− 2187.866	− 920.389

[a]The $V_{0,A}$ values are primarily from Tables 1 and 2

[b]Reference [57]
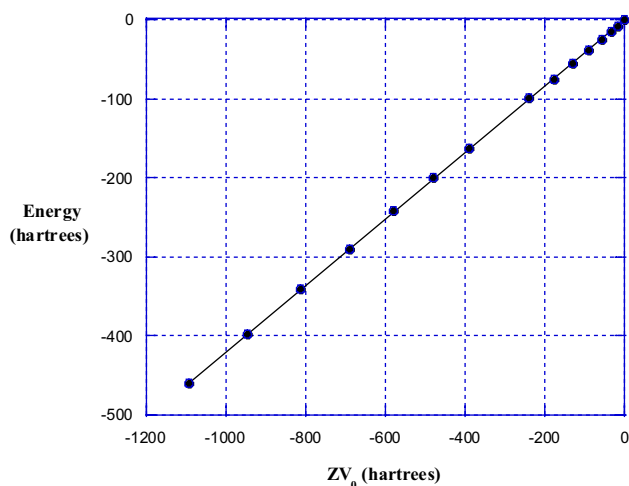
Fig. 2 Relationship between exact atomic energy and product ZV_0 for atoms in Table 3. $R^2 = 1.0000$

58–60], which was a predecessor of Hohenberg–Kohn density functional theory; the Thomas–Fermi formula is,

$$E_{atom} = \frac{3}{7}(ZV_0) = 0.4286(ZV_0) \tag{7}$$

Fraga showed that when Hartree–Fock V_0 are used, Eq. (7) reproduces true atomic energies to within about 2% [61].

It was later demonstrated that Eq. (7) could be extended to molecules [62]:
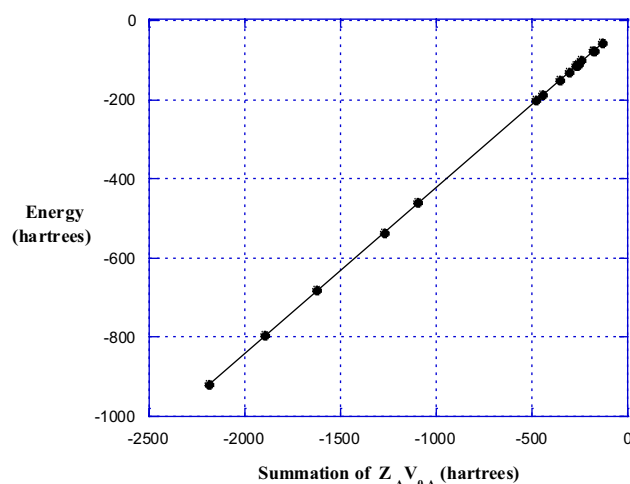
Fig. 3 Relationship between exact molecular energy and $\sum_A Z_A V_{0,A}$ for molecules in Table 4. $R^2 = 1.0000$

$$E_{mol} = \frac{3}{7}\left(\sum_A Z_A V_{0,A}\right) = 0.4286\left(\sum_A Z_A V_{0,A}\right) \tag{8}$$

With Hartree–Fock $V_{0,A}$, the errors are usually less than 2%.

Significantly better atomic and molecular energies are obtained with eqs. (5) and (6) and using the V_0 and $V_{0,A}$ computed at our present B3P86/6–311 + G(3df,2p) level. For the atoms in Table 3, the average deviation from the exact energies is 0.89%; for the molecules in Table 4, it is 0.44%. While these errors are too large to allow reliable calculations of energy differences, e.g., dissociation energies, the results do indicate that eqs. (5) and (6) provide qualitatively meaningful atomic and molecular energies.

Both the rigorous molecular energy formula, Eq. (3), and the correlation in Eq. (6) express molecular energy entirely as a sum of atomic contributions. This suggests, as proposed some time ago [63], that the energy of a molecule can be apportioned between its constituent atoms in accordance with the ratio of each atom's contribution to the sum of the contributions of all of the atoms. By that reasoning, the energy of atom M in the molecule is,

$$E_{atom,M} = \left[\frac{Z_M V_{0,M}}{\sum_A Z_A V_{0,A}}\right] E_{mol} \tag{9}$$

Using the data in Tables 3 and 4, we have calculated the energies $E_{atom,M}$ of the atoms in the molecules in Table 4. They are listed in Table 5. We have also found the differences ΔE between the energies of the atoms in the molecules and the free atoms, Eq. (10); these are also in Table 5.

Table 5 Calculated energies $E_{atom,M}$ of atoms M in molecules, Eq. (9), and energy differences ΔE, Eq. (10)

Molecule	Atom M	$E_{atom,M}$ (hartrees)	ΔE(hartrees)
NH_3	N	− 55.198	− 0.609
	H	− 0.455	0.045
C_2	C	− 37.962	− 0.117
H_2O	O	− 75.595	− 0.527
	H	− 0.423	0.077
HF	F	− 100.075	− 0.341
	H	− 0.385	0.115
N_2	N	− 54.771	− 0.182
CO	C	− 37.518	0.327
	O	− 75.809	− 0.741
$H_2C{=}O$	C	− 37.495	0.350
	O	− 76.095	− 1.027
	H	− 0.460	0.040
HNO	N	− 54.348	0.241
	O	− 75.701	− 0.633
	H	− 0.436	0.064
O_2	O	− 75.164	− 0.096
CO_2	C	− 37.194	0.651
	O	− 75.703	− 0.635
F_2	F	− 99.765	− 0.031
HCl	Cl	− 460.417	− 0.269
	H	− 0.399	0.101
ClO	Cl	− 460.252	− 0.104
	O	− 75.068	0.000
P_2	P	− 341.352	− 0.093
S_2	S	− 398.192	− 0.082
Cl_2	Cl	− 460.195	− 0.047

$$\Delta E = E_{atom,M} - E_{atom} \tag{10}$$

For homonuclear diatomics, each $E_{atom,M}$ is simply half of E_{mol}. It also follows from eqs. (9) and (10) that the sum of the ΔE for any molecule equals the atomization energy of that molecule, i.e., the energy needed to separate it into its constituent free atoms. For diatomics, this is the dissociation energy. Since we used the exact E_{atom} and E_{mol} in eqs. (9) and (10), the sums of the ΔE in Table 5 must equal the exact atomization or dissociation energies of the molecules.

When an atom has $\Delta E < 0$ in a particular molecule, its energy in that molecule is more negative than in the free state; $\Delta E > 0$ indicates that the atom's energy in the molecule is less negative than as a free atom. To some extent, the signs of the ΔE can be linked to the atoms' electronegativities, the more electronegative having the more negative ΔE, but as with the $V_{0,A}$ values discussed earlier, the relationship to electronegativity is limited. Note, for instance, that in ClO the oxygen has $\Delta E = 0.000$, while the ΔE of the chlorine is − 0.104 (Table 5).

5 Discussion and summary

The electrostatic potential at the nucleus of an atom A, labeled V_0 for the free atom and $V_{0,A}$ when the atom is part of a molecule, is a key property of that atom. Its value changes remarkably little in going from one environment to another–free atom to nonpolar covalent to polar covalent to ionic–even though its nuclear and electronic components separately may vary considerably. The changes in these components largely cancel. The electrostatic potential at the nucleus can thus be viewed as qualitatively characterizing the atom, as shown in Table 1 and Fig. 1.

These observations bring to mind the "Quantum Chemical le Chatelier Principle" formulated by Mezey [64–66]. This states that when a molecule at equilibrium is subjected to a perturbation, such as a change in conformation, the effects upon the nuclear repulsion and electronic energies may be quite considerable but of similar magnitudes and opposite signs, so that they will approximately cancel. The total energy is relatively little affected.

The energies of atoms and molecules can be formulated, both rigorously and approximately, in terms of the electrostatic potentials at their nuclei. The molecular expressions are simply summations over the atomic contributions; there are no explicit interatomic ones. This provides a seemingly reasonable basis for estimating the energies of atoms in molecules.

We do not claim that the results that have been presented demonstrate conclusively the existence of atoms in molecules. It may be that this will never be definitively proven. However, a concept does not have to be rigorously established in order to be very useful, e.g., the laws of thermodynamics. It seems fair to say that our results provide strong indications that it is meaningful to view molecules and polyatomic ions as composed of atoms that keep their identities.

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