Theor Chem Acc (2006) 116: 450–455
DOI 10.1007/s00214-006-0097-1

REGULAR ISSUE

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Ionisation potential, electron affinity and polar bond: a first-order correction method for interaction energy

Received: 26 November 2004 / Accepted: 6 April 2005 / Published online: 14 February 2006

Abstract A new first-order method is proposed to improve the potential energy of the polar molecules. The nature of the polar bonding is illustrated by some examples, LiF, LiO, LiH, ScO, and AlO molecules, covering from strong to weak ionic cases. A simple first-order correction method using the dipole moment or the effective charge, and the experimental and theoretical ionisation potentials and electron affinities is explained. Application of this method to those molecules improves remarkably the spectroscopic constants. This method can be easily extended to polyatomic cases involving a polar bonding between an electropositive moiety (electron donor) and an electronegative functional group (electron acceptor).

Keywords Polar bonding · Electron donor and acceptor · Ionic and covalent coupling · Ionisation potential and electron affinity · First-order correction

1 Introduction

Ab initio quantum chemical calculation of the polar diatomic molecule, in general, does not give sufficiently accurate potential energies. The bond strength is often underestimated and the ionic–covalent avoided crossing regions are given for shorter distances, i.e. the potential surface is not good enough. In many cases, it is a consequence of the underestimation of the electron affinity for the electronegative (or electron acceptor) atom. The ionisation potential of the electropositive (electron donor) atom, on the other hand, is less difficult to reproduce by calculation. Indeed, the electron correlation effect increases as the number of valence electron increases, and the appropriate treatment evenly covering the neutral, cationic, and anionic species at the same time requires a high-order coupled-cluster or configuration interaction method. So, it is necessary to amend the error by adding a correction term. This is also the case for polyatomic molecules involving a polar bonding between an electron donor and an electron acceptor, either they are atoms or functional groups.

Higher energy of the ionic configuration with respect to the covalent configuration is also visible in the quantum chemical calculation for the substitution reaction, e.g. the oxidation reactions. The calculation often gives higher activation barriers vis-à-vis the experimental data. In this work, a simple first-order correction method is proposed to amend this kind of errors. First, the nature of the polar bond will be illustrated by a moderately ionic case in the example of LiH molecule. Then the first-order correction method will be explained. The application of this method to a strong ionic case (LiF) and some monoxides (LiO, AlO, ScO) remarkably improves the spectroscopic constants.

There has been much study on the relationship between the bond energy and the atomic state in the molecule since the early times of quantum chemistry [1–4]. Although, it is strictly impossible to define the atomic state in the molecule, it is interesting to analyse the molecular state in terms of the atomic states from the intuitive point of view. Recent studies report an attempt to deduce the potential energy curves from the atomic valence state theory using the empirical electronegativities and some other empirical parameters [5,6]. The present work differs from those studies. We use ab initio calculations to obtain the weight of the ionic contribution in the molecular wavefunction. The experimental ionisation potentials and electron affinities are used to compensate the small error of the ab initio calculation.

2 Theoretical background: ionic and covalent mixing

The chemical bond between two atoms can be analysed by a two-state problem. Let us consider a basis in two dimensions: $\{|\Psi_n\rangle, |\Psi_i\rangle\}$ consisting in two wavefunctions, covalent and ionic. Each wavefunction, in general, can be developed in a large number of configuration state functions. The electron

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wavefunction representing the chemical bond can then be written as $\Phi = c_n\Psi_n + c_i\Psi_i$ with $|\langle\Psi_n|\Psi_i\rangle| = s \neq 0$ because the basis is nonorthogonal. We assume here that Φ is normalised, i.e.

$$|c_n|^2 + |c_i|^2 + 2s\,\mathrm{Re}\left\{c_n^* c_i\right\} = 1.$$

Let us put here

$$\langle\Psi_n|\,H\,|\Psi_n\rangle = w_n, \quad \langle\Psi_i|\,H\,|\Psi_i\rangle = w_i,$$
$$\langle\Psi_i|\,H\,|\Psi_n\rangle = v_{in} = \langle\Psi_n|\,H\,|\Psi_i\rangle^*.$$

The first and second terms represent the diagonal hamiltonian matrix elements, and the third term represents a crossed hamiltonian matrix element. For large internuclear distances, the crossed term tends to zero except for the avoided crossing distance. This term is often called the diabatic coupling term. The mean value of the energy, apart from the nuclear repulsion term, becomes

$$W = \langle\Phi|\,H\,|\Phi\rangle = |c_n|^2 w_n + |c_i|^2 w_i + 2\,\mathrm{Re}\left\{c_i^* c_n v_{in}\right\}. \quad (1)$$

For large internuclear distances, the energy tends to either w_n or w_i as the state becomes entirely covalent or ionic. For small internuclear distances the crossed term, the third one in (1), is not negligible.

The dipole moment of the molecule can be differentiated into two contributions, the nuclear part ($\vec{d}_\mathrm{N}$) and the electronic part ($\vec{d}_\mathrm{e}$). The mean value of the dipole moment becomes

$$\begin{aligned}\vec{d} &= \langle\Phi|\,\vec{\mu}_\mathrm{e}\,|\Phi\rangle + \vec{d}_\mathrm{N}\\ &= |c_n|^2\left\{\langle\Psi_n|\,\vec{\mu}_\mathrm{e}\,|\Psi_n\rangle + \vec{d}_\mathrm{N}\right\} + |c_i|^2\left\{\langle\Psi_i|\,\vec{\mu}_\mathrm{e}\,|\Psi_i\rangle + \vec{d}_\mathrm{N}\right\}\\ &\quad +2\,\mathrm{Re}\left\{c_i^* c_n\left(\langle\Psi_i|\,\vec{\mu}_\mathrm{e}\,|\Psi_n\rangle + s\vec{d}_\mathrm{N}\right)\right\}\end{aligned}$$

where $\vec{\mu}_\mathrm{e}$ is the electronic dipole moment operator. The first term containing the covalent wavefunction becomes zero for the electrically neutral systems. Then the dipole moment becomes

$$\begin{aligned}\vec{d} &= |c_i|^2\left\{\langle\Psi_i|\vec{\mu}_\mathrm{e}|\Psi_i\rangle + \vec{d}_\mathrm{N}\right\}\\ &\quad +2\,\mathrm{Re}\left\{c_i^* c_n\left(\langle\Psi_i|\vec{\mu}_\mathrm{e}|\Psi_n\rangle + s\vec{d}_\mathrm{N}\right)\right\}\end{aligned} \quad (2)$$

For large internuclear distances, either of the coefficients, c_n or c_i should tend to zero as the state becomes either entirely covalent or entirely ionic. (The integral $\langle\Psi_i|\,\vec{\mu}_\mathrm{e}\,|\Psi_n\rangle$ tends to the transition dipole moment for large distances except for the avoided crossing point.) So for large internuclear distances, the dipole moment becomes either zero for neutral state or

$$\vec{d} \approx |c_i|^2\left(\langle\Psi_i|\,\vec{\mu}_\mathrm{e}\,|\Psi_i\rangle + \vec{d}_\mathrm{N}\right) = \pm|c_i|^2 eR\hat{z} \quad (3)$$

for ionic state where e is the elementary charge, R is the internuclear distance, and $\hat{z}$ is a unit vector along the bond axis.

In this case, $\Delta = w_i - w_n$ represents the difference between the ionization potential (IP) of the donor atom and the electron affinity (EA) of the acceptor atom, i.e.

$$\Delta = \mathrm{IP(D)} - \mathrm{EA(A)}. \quad (4)$$

Then the Eq. (1) can be transformed to

$$W = \left\{|c_n|^2 + |c_i|^2\right\}w_n + |c_i|^2\Delta + 2\,\mathrm{Re}\left\{c_i^* c_n v_{in}\right\} \quad (5)$$

Taking the expression for $|c_i|^2$ from (3), we know that the second term of (1) or (5) becomes $Q\Delta$, where Q, i.e. the dipole moment divided by the elementary charge and the internuclear distance,

$$Q = \frac{d}{eR}, \quad (6)$$

is an effective charge (in atomic units, Q is a dimensionless number). So, we know that the bond energy should contain a term directly proportional to the difference between the ionisation potential and the electron affinity. The bond energy also contains a crossed term, the third term in Eq. (1) or (5). The atomic electron affinities have been recently collected in a review paper [7].

3 Ionic and covalent mixing in the LiH molecule

The LiH molecule used to be a good pedagogical example to show the coupling between the covalent and ionic configurations. It has been studied recently by laser spectroscopy and quantum chemical calculations [8,9]. The $^1\Sigma^+$ electronic states dissociating into from $2s+1s$ to $4f+1s$ and $\mathrm{Li^+H^-}$ are calculated in multi-reference (MR) configuration interaction (CI) method using the MOLCAS program package [10]. The computational details, like the primitive Gaussian type orbitals (GTOs), the atomic basis functions (ABFs), the active space for the multiconfiguration (MC) self-consistent field (SCF) calculation, the active space for the singles and doubles substitutions, the restricted space to allow only single substitutions, the total number of configuration state functions (CSFs) in the MRCI, etc., were explained in a previous work [11]. The potential energy curves (PECs) for those $^1\Sigma^+$ states are reported in Fig. 1. Only the $^1\Sigma^+$ symmetry states can include the ionic configurations and we gave here only four states for clarity. We can see in this figure that the ionic contribution perturbs all electronic states appearing in this figure. The energy level of the ionic state at infinite separation ($R = \infty$), i.e. Δ with respect to the energy level of $2s + 1s$, lies between the $4f + 1s$ and $5s + 1s$, so the $5s + 1s$ electronic state and higher states are unperturbed by the ionic contribution, $\mathrm{Li^+(^1S)}$+$\mathrm{H^-(^1S)}$. The ionic–covalent coupling is very large for the $2s + 1s/2p + 1s$ and $2p + 1s/3s + 1s$ pair states, i.e. the coupling occurs for a large interval of the internuclear distance and the splittings between these pair states are very large in comparison to the thermal energy. However, the coupling strength decreases for higher states, and the ionic part follows closely the point-charge dipole energy ($\Delta - R^{-1}$) curve (dotted in Fig. 1) for the $3s + 1s$ and

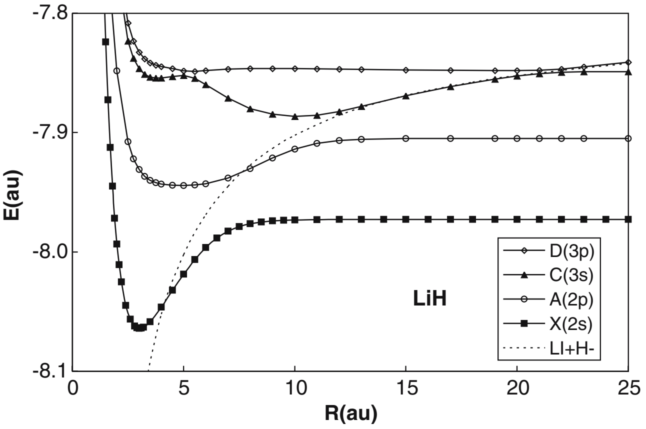

Fig. 1 Potential energy curves of the low-lying ${}^1\Sigma^+$ electronic states of LiH. *Dotted curve* in $(\Delta - R^{-1})$ is the point-charge dipole curve (see text)

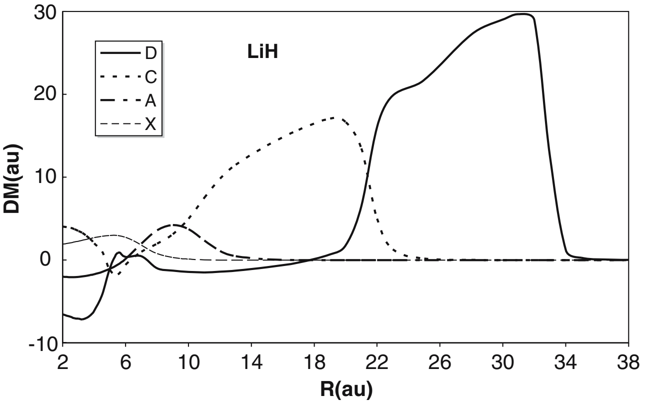

Fig. 2 Dipole moments of the $1^1\Sigma^+(\mathrm{X}), 2^1\Sigma^+(\mathrm{A}), 3^1\Sigma^+(\mathrm{C})$, and $4^1\Sigma^+(\mathrm{D})$ states of Li

higher states. The maximum deviation between the ab intio PEC and the point charge dipole curve is less than $2\,\mathrm{cm}^{-1}$ for $R > 40\,\mathrm{bohr}$, less than $-50\,\mathrm{cm}^{-1}$ for $R > 30\,\mathrm{bohr}$, and less than $-85\,\mathrm{cm}^{-1}$ for $R > 25\,\mathrm{bohr}$. And the energy splitting due to the ionic–covalent coupling is small and the avoided crossing occurs in a very localized way for high-lying electronic states. The energy splittings (ΔE_{X}) and crossing distances (R_{X}) are, respectively, $1.1\,\mathrm{cm}^{-1}$ for 212.5 bohr in the $4f + 1s$ state, $1.9\,\mathrm{cm}^{-1}$ for 211.1 bohr in the $4d + 1s$ state, $0.4\,\mathrm{cm}^{-1}$ for 183.65 bohr in the $4p + 1s$ state, $0.2\,\mathrm{cm}^{-1}$ for 82.59 bohr in the $4s + 1s$ state, $59.9\,\mathrm{cm}^{-1}$ for 34.5 bohr in the $3d + 1s$ state, $118.5\,\mathrm{cm}^{-1}$ for 33.0 bohr in the $3p + 1s$ state.

The dipole moments for the $1^1\Sigma^+(\mathrm{X}), 2^1\Sigma^+(\mathrm{A})$, $3^1\Sigma^+(\mathrm{C})$ and $4^1\Sigma^+(\mathrm{D})$ states are reported in Fig. 2, and the effective charges of those states are reported in Fig. 3. The last figure shows particularly well the avoided crossings in cascade between the covalent configurations and the ionic configurations.We can also observe that the effective charge for the ionic part increases with the degree of excitation: the effective charge of the D state is larger than that of C state which in its turn is larger than that of the A state, etc.

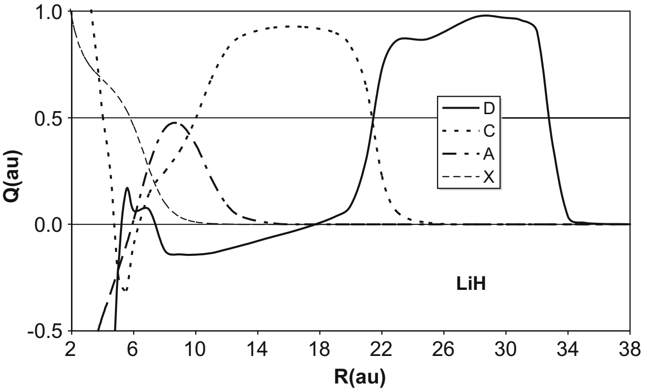

Fig. 3 Effective charges of the $1^1\Sigma^+(\mathrm{X}), 2^1\Sigma^+(\mathrm{A}), 3^1\Sigma^+(\mathrm{C})$, and $4^1\Sigma^+(\mathrm{D})$ states of Li

The asymptotic energy levels of the reported electronic states, i.e. the energy at infinite separation ($R = \infty$), are reported in Table 1. Our calculated values for the homolytic (diradical in this case) separation are very good in comparison with the experimental data, the largest deviation being $58\,\mathrm{cm}^{-1}$ for the $2p + 1s$ and the deviations are less than $10\,\mathrm{cm}^{-1}$ for the $3d + 1s$ and higher states, as we have reported before [11]. However, the heterolytic separation (or ionic asymptote), $\mathrm{Li}^+({}^1\mathrm{S}) + \mathrm{H}^-({}^1\mathrm{S})$, is too much higher than the experimental data by $246\,\mathrm{cm}^{-1}$ if we took the electron affinity as $6,083\,\mathrm{cm}^{-1}$ [12]. This is due to the difficulty of calculating the electron affinity, while our calculated ionisation potential is only $46\,\mathrm{cm}^{-1}$ smaller than the experimental value, $43,487\,\mathrm{cm}^{-1}$ [13]. It means that Fig. 1 includes the error on the Δ, i.e. we overestimate this by $200\,\mathrm{cm}^{-1}$ ($37,604\,\mathrm{cm}^{-1}$ instead of the experimental value, $37,404\,\mathrm{cm}^{-1}$). The consequence of this would be the overestimation of the PEC for the ionic part of the $3p + 1s$ and higher states.

The ionic parts of those high-lying states show the effective charges close to 1 which means they are fully ionic. We could compensate the error for their potential energies by lowering the ionic part of the PECs by the computed error in Δ. However, the ionic parts of the PECs for short distances are not fully ionic but partially ionic as it can be seen by the effective charges (Fig. 3). So, we arrive at a considerable dilemma.

4 First-order correction

The analysis of the LiH case allows to propose the best first-order (which means using the properties derived from the zeroth wavefunction) correction which is

$$E'(R) = E(R) + (\Delta_{\mathrm{th}} - \Delta_{\mathrm{exp}\,er}) \times Q(R) \qquad (7)$$

where the $E(R)$ is the initial ab intio PEC and $E'(R)$ is the corrected PEC. The asymptotic behaviour of the ionic part of the PECs should be correct after applying this formula because $Q \approx 1$. For shorter distances, the correction should

Table 1 Ionisation energies of LiH at infinity (in cm^{-1})

States	Experimental[a]	Theoretical	Errors
Li^+/H(1s)	0	0	0
5p + H	4,471	4,464	7
5s + H	5,187	5,185	2
$\mathrm{Li}^+/\mathrm{H}^-$	6,083[b]	5,837	246
4f + H	6,857	6,847	10
4d + H	6,864	6,854	10
4p + H	7,017	7,009	8
4s + H	8,475	8,471	4
3d + H	12,204	12,200	4
3p + H	12,562	12,543	19
3s + H	16,281	16,271	10
2p + H	28,583	28,525	58
2s + H	43,487	43,441	46

[a] From Ref. [13]
[b] From Ref. [12]

Table 2 Spectroscopic constants of the ground state of LiH

	From $E(R)$	From $E'(R)$	Experimental [a]
R_e(pm)	159.9	159.8	159.5584
$D_\mathrm{e}(\mathrm{cm}^{-1})$	20,027	20,179	20287.7
$\omega_\mathrm{e}(\mathrm{cm}^{-1})$	1,399	1,401	1405.5

[a] From Ref. [23]

be smaller and the main result would be lowering the PEC by a fraction (Q) of the error in Δ. This correction concerns the diagonal part of the energy in (1) or (5) and does not take into account the crossed term, the last term of (1) or (5). The expression (7) contains both the theoretical first-order properties and the experimental data, so it can be qualified as a semi-empirical correction formula.

Now let us see if this proposed correction improves the calculated spectroscopic properties. In Table 2 are summarized the spectroscopic constants of the ground state of LiH. In comparing the constants before correction and after correction, it appears that the bond energy is increased to closely match the experimental value. On the other hand, the equilibrium distance and the harmonic frequency have little changed. In fact, the latter two quantities are related to the variation of the effective charge around the equilibrium bond length and the small change in those quantities comes from a slow variation of the effective charge. This result shows that our proposed method improves the bond energy remarkably.

5 Ionic and covalent mixing in the LiF molecule

The ground state of the LiF molecule is known to be strongly ionic as can be inferred from the large electron affinity of the fluorine atom, 3.4012 eV [14]. The avoided crossings between the ground state and the excited states of the same symmetry ($^1\Sigma^+$) have been much discussed in literature. We have calculated the seven lowest $^1\Sigma^+$ electron states with MRCI method [15]. The result shows two avoided crossings, one occurring between the 1 and 2 $^1\Sigma^+$ states, and the second occurring between the 2 and 3 $^1\Sigma^+$ states. The effective charges, defined in (6), of these three states as functions of the internuclear distance clearly show the covalent and ionic parts of those states. The heterolytic dissociation asymptote, $\mathrm{Li}^+ + \mathrm{F}^-$, lies between the Li(2p) + F and Li(3s) + F homolytic dissociation asymptotes according to the experimental data shown in Table 3. While our molecular calculation gives correct order for the asymptotes, and while our calculated neutral energy levels are in good agreement with the experimental values, the calculated ionic energy level appears to be much too high (by nearly 1 eV) in comparison with the experiment. It means that the ionic part should be much lowered to reproduce the experimental PECs. If we compared our calculated spectroscopic constants of the ground state with the experimental data in Table 4, we can find that there is a general agreement so that the calculation could be considered as satisfactory. However, the inaccuracy of the ionic asymptote makes the calculated avoided crossing distances far too short with respect to the real ones, which means that the PECs are totally erroneous for medium and large internuclear distances. Bauschlicher and Langhoff [16] have done a full CI calculation with a $9s4p$ GTOs contracted to $4s2p$ ABFs for Li and $9s6p1d$ GTOs contracted to $4s3p1d$ ABFs for F. Their spectroscopic constants for the ground state are: 3.090 bohr (1.635 A) for the R_e, 5.249 eV for the D_e and 840 cm^{-1} for the ω_e and 2.731 au for the μ_e (our calculation gave 2.537 au for the dipole moment, which means 0.846 for the effective charge). It means that the full CI with a limited atomic basis set does not give satisfactory spectroscopic constants, either.

The spectroscopic constants of the ground state after correcting the initial PEC in Table 4 shows that the present proposed method is efficient for improving the bond dissociation energy, while the bond distance and the harmonic vibrational frequency changed little.

6 Ground states of monoxides: LiO, AlO, and ScO molecules

The ground and excited states of some monoxides, LiO, AlO [17], and ScO [18], were calculated. For the LiO molecule, we have used a method similar to what we have done for the LiF calculation. In our molecular calculation of the ScO molecule, we have calculated only the lowest three doublet states (ScO) including the ground state. In fact, it is not possible

Table 3 Ionisation energies of LiF at infinity (in eV)

States	Experimental[a]	Theoretical	Errors
Li^+/F	0	0	0
4s + F	1.0113	1.0509	0.0396
3d + F	1.5132	1.4723	0.0391
3p + F	1.5575	1.5149	0.0426
3s + F	2.0186	1.9804	0.0382
$\mathrm{Li}^+/\mathrm{F}^-$	3.4012[b]	2.4233	0.9779
2p + F	3.5439	3.4963	0.0476
2s + F	5.3917	5.3606	0.0311

[a] From Ref. [13]
[b] From Ref. [14]

Table 4 Spectroscopic constants of the ground state of LiF

	From $E(R)$	From $E'(R)$	Experimental
R_e(pm)	156.3	156.4	156.3864 [a]
D_e(eV)	5.192	6.003	6.018 [a,b]
ω_e(cm^{-1})	922	919	910.34 [a]

[a] From Ref. [24]
[b] From Ref. [25]

for the time being to calculate all electronic states dissociating up to the $Sc^+ + O^-$ asymptote because we need to include in our MRCI calculation a great number of the states having the $^2\Sigma^+$ symmetry. Instead, we have done a separate atomic calculation where we have used the same atomic basis as in the molecular case and the same level of MRCI. The same was the case for the AlO molecule. In LiO molecule, however, we have calculated four $^2\Pi$ states and could obtain the ionic state at infinity, $Li^+ + O^-$, directly from the molecular calculation. The differences between the ionisation potentials of the metal atoms and the electron affinity of the oxygen atom are reported in Table 5. The spectroscopic constants calculated from the MRCI calculations and those calculated from the corrected potential curves are reported in Table 6. This table also shows a remarkable improvement for the bond energy, while the bond distance and the harmonic vibrational frequency have little changed. It is clear that our proposed method also works well for monoxides.

The ionicity (or polarity) of the ground state depends not only on the electrophilic atomic species but also on the IP(D) − EA(A). If we defined the ionicity of the polar bonding according to the effective charge of the donor atom (or negative of that of acceptor atom), the ionicity of the ground state ($X^2\Sigma^+$) of the ScO molecule would be weaker than that of the LiH (rather unexpectedly) or that of the LiF (expectedly). Indeed, the effective charges around the equilibrium bond length (R_e) of the molecules presented in this work are: 0.57 in AlO, 0.68 in ScO, 0.76 in LiH, 0.82 in LiO, and 0.85 in LiF. If we compared those with the calculated Δ s (or experimental Δ s in parentheses), they are respectively: 5.4990 (5.1004) for ScO, 4.9288 (4.5247) for AlO, 4.6622 (4.6374) for LiH, 4.3029 (3.9304) for LiO, and 2.9373 (1.9905) for LiF, in eV. So we see that although there is a weak correlation between the ionicity and the Δ, such correlation is not so much quantitative. (In fact, the discrepancy in these cases can be partially explained by differentiating the σ and π bonds.) On the other hand, the ionicity also depends on the degree of excitation. Smaller the ionic energy level in comparison with the neutral (covalent) energy level ($IP_n(D) - EA(A)$) is (where the index n is to differentiate the ground and excited electronic states of the electron donor), larger will be the polarity.

Table 5 Ionisation potentials and electron affinities for LiO, AlO, and ScO (in eV)

Molecules	Δ E	Experimental	Theoretical	Errors
LiO	IP (Li) − EA (O)	3.9304 [a,b]	4.3029	0.3725
AlO	IP (Al)	5.9858 [a]	5.9161	0.0697
	EA (O)	1.4611 [b]	0.9873	0.4738
	IP (Li) − EA (O)	4.5247	4.9288	0.4041
ScO	IP (Sc)	6.5615 [a]	6.3512	0.2103
	EA (O)	1.4611 [b]	0.8522	0.6089
	IP (Li) − EA (O)	5.1004	5.4990	0.3986

[a] From Ref. [13]
[b] From Ref. [26]

Table 6 Spectroscopic constants of the ground states of LiO, AlO, and ScO

Molecules	Constants	From $E(R)$	From $E'(R)$	Experimental
LiO	R_e (pm)	170.2	170.0	169.5 [a]
	D_0 (cm^{-1})	3.329	3.625	3.647
	ω_e (cm^{-1})	801	804	851.5 [a]
AlO	R_e (pm)	163.5	163.2	161.79 [a]
	D_0 (cm^{-1})	4.861	5.092	5.27 [b]
	ω_e (cm^{-1})	968	981	979.23 [a]
ScO	R_e (pm)	1.688	1.692	1.66826 [a]
	D_0 (cm^{-1})	6.617	6.887	6.92 [c]
	ω_e (cm^{-1})	976	988	964.95 [a]

[a] From Ref. [24]
[b] From Ref. [27]
[c] From Ref. [21]

7 Conclusion

This study confirmed the fact that the accurate description of the atomic energy levels and the electron affinity is crucial to calculate the potential energy curves for the polar diatomic molecules. It also showed that a good measure of the ionicity or polarity is not the atomic species but rather the ionic energy level in comparison with the neutral (covalent) energy level, IP(D) − EA(A). Our work showed that not only reasonable error (in most cases we presented here) but also unreasonable error (in the LiF case) in the calculated energy difference, IP(D) − EA(A), can be compensated by adding our proposed first-order correction energy using a zeroth-order property (dipole moment or effective charge).

Another important aspect of this method is the correction of the ionic–covalent crossing distance, R_x. This distance is directly connected with the reactive cross section (πR_x^2) according to the harpoon mechanism. As a result, the reactive cross section can change a lot after this correction. In many three-body chemical reactions are also involved in the ionic–covalent couplings. We have recently studied some oxidation reactions like $Sc + NO \rightarrow ScO + N$ [18–20], $Sc + O_2 \rightarrow ScO + O$ [18], $Ti + O_2 \rightarrow TiO + O$ [21], and $Al + O_2 \rightarrow AlO + O$ [17]. In each case, our calculated activation barrier was higher than the experimental value. As the activation barrier is a result of the ionic–covalent coupling, its height and geometrical parameter are sensitive to the appropriate mixture between these two configurations. Our present method corrects the activation barrier to lower its height and the geometrical parameter for the transition state is corrected to a larger distance. Those interesting aspects will be discussed in more detail in the near future. We are also going to study the extension of this method to larger polyatomic molecules containing an electron donor moiety and an electron acceptor group.

The accurate reproduction of the ionisation potential and the electron affinity is also important for the homopolar dimmers, which are not polar at all. The resonant ionic configurations are present in the electronic states of the alkali dimers as it was reported in the Na_2 case [22]. Also in this case, accurate potential energy curves can be obtained only with a method which can reproduce those atomic energies accurately.

Acknowledgements It is a great pleasure for me to dedicate this paper in honour of Dr. Jean-Paul Malrieu, as one of his former PhD students, on the occasion of his official retirement. I hope he will still work for many years to contribute to the advancement of the theoretical chemistry. I would like to thank Prof. Laszló von Szentpály for many of his useful discussions.

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