Theor Chim Acta (1987) 72: 197-205

Theoretica
Chimica Acta

A modification of Koopmans' theorem by imposition of the virial theorem in molecules

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(Received September 11, 1986, revised March 23, 1987/Accepted April 29, 1987

Imposition of the virial theorem on Koopmans' theorem permits the introduction of some relaxation effect in the electronic cloud of atomic (less than 5%) or molecular (less than 1.3% for the systems studied) systems and a partitioning of the ionization energy. The method is applied in some diatomic hydrides. It is observed that the imposition of the virial theorem improves the ionization of the innermost molecular orbitals significantly, while the improvement is negligible for the outermost orbitals. The ionization energy is divided among three different terms that elucidate some aspects of the nature of the ionization process.

Key words: Virial theorem — Koopmans' theorem — Relaxation — Partition of the ionization energy — Molecules

1. Introduction

A simple way to estimate ionization energies (I_i) is to subtract the total energy of a neutral atom or molecule (E) from the total energy of the created cation (E^+):

$$I_i = E^+ - E \tag{1}$$

The large magnitude of each energy on the right-hand side of Eq. (1) makes it difficult to apply the equation when using the Hartree-Fock-Roothaan method. It is common practice to invoke Koopmans' theorem [1] to approximate I_i:

$$I_i = -\varepsilon_i \tag{2}$$

where ε_i is the orbital energy from which an electron is removed. The deficiencies of Koopmans' theorem are well known, and a set of methods [2-4] has been used to improve the calculated energies. These improvements are based on the inclusion of the relaxation and correlation effects.

One simple way of improving Koopmans' theorem is based on the virial theorem [5]. Koopmans' theorem assumes that geometry and orbitals are "frozen" before and after ionization. This implies that even if the virial theorem is complied with for the starting wave function of the neutral molecule, it will be violated for the wave function of the ionized one. Scaling methods [5] applied in frozen cations of atomic systems have shown interesting results [6-8]. Besides the improvement of the ionization energies, this method permits the extraction of information on the electronic structure. It is also possible to verify that scaling introduces some relaxation (less than 5%) in electronic cloud. The quantity of reorganization introduced depends on the type of atoms as well as the atomic orbital. The objective of this work is to generalize the method [6] for polyatomic systems and to study its consequences in some diatomic hydrides.

2. Method

In this work, Löwdin's notation for scaled and unscaled energies is used. $X(\eta, \boldsymbol{R}, \theta)$ and $X(1, \boldsymbol{\rho}, \boldsymbol{\theta})$ represent the energy X with and without scaling, respectively; $\boldsymbol{R}$ and $\boldsymbol{\theta}$ are the sets of l-bond lengths and κ-bond angles of molecular systems; $\boldsymbol{\rho}$ is related to $\boldsymbol{R}$ by:

$$\boldsymbol{\rho} = \eta \cdot \boldsymbol{R} \tag{3}$$

where η is the scaling parameter for molecular systems. It can be calculated [5] from:

$$\eta = -\left[\frac{V(1, \boldsymbol{\rho}, \boldsymbol{\theta}) + \sum_l \rho_l \cdot \dfrac{\partial V(1, \boldsymbol{\rho}, \boldsymbol{\theta})}{\partial \rho_l}}{2 \cdot T(1, \boldsymbol{\rho}, \boldsymbol{\theta}) + \sum_l \rho_l \cdot \dfrac{\partial T(1, \boldsymbol{\rho}, \boldsymbol{\theta})}{\partial \rho_l}}\right]. \tag{4}$$

Here V and T are the potential and kinetic energies of the neutral molecular system in question.

A general situation would be that the initial and final molecular wave functions do not comply with the virial theorem. Then, the scaling method must be used twice, first for the neutral molecule and second for the frozen cation. Using the η of Eq. (4) we obtain the following scaled energies with any geometry [5]:

$$E(\eta, \boldsymbol{R}, \boldsymbol{\theta}) = T(\eta, \boldsymbol{R}, \boldsymbol{\theta}) + V(\eta, \boldsymbol{R}, \boldsymbol{\theta}) \tag{5}$$

$$T(\eta, \mathbf{R}, \boldsymbol{\theta}) = \eta^2 \cdot T(1, \boldsymbol{\rho}, \boldsymbol{\theta}) = \sum_i \eta^2 \cdot t_i(1, \boldsymbol{\rho}, \boldsymbol{\theta}) = \sum_i t_i(\eta, \mathbf{R}, \boldsymbol{\theta}) \tag{6}$$

$$V(\eta, \mathbf{R}, \boldsymbol{\theta}) = \eta \cdot V(1, \boldsymbol{\rho}, \boldsymbol{\theta}) = \eta \cdot [E(1, \boldsymbol{\rho}, \boldsymbol{\theta}) - T(1, \boldsymbol{\rho}, \boldsymbol{\theta})]. \tag{7}$$

According to Nelander [9], the scaled energies in Eqs. (5), (6), and (7) satisfy the virial theorem for polyatomic molecules:

$$E(\eta, \mathbf{R}, \boldsymbol{\theta}) = -T(\eta, \mathbf{R}, \boldsymbol{\theta}) - \sum_{l} \rho_l \cdot \frac{\partial E(\eta, \mathbf{R}, \boldsymbol{\theta})}{\partial \rho_l}. \tag{8}$$

It can be shown that the scaled orbital energy takes the form of equation:

$$\varepsilon_i(\eta, \mathbf{R}, \boldsymbol{\theta}) = \eta \cdot [(\eta - 1) \cdot t_i(1, \boldsymbol{\rho}, \boldsymbol{\theta}) + \varepsilon_i(1, \boldsymbol{\rho}, \boldsymbol{\theta})], \tag{9}$$

where t_i is the kinetic energy of the ith molecular orbital. Substitution of Eq. (9) into Eq. (2) provides corrected Koopmans' ionization energies.

Cation energies can be derived using the scaled quantities of the neutral molecule:

$$T^{+}(1, \boldsymbol{\rho}, \boldsymbol{\theta}) = T(\eta, \boldsymbol{R}, \boldsymbol{\theta}) - t_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}) \equiv T^{+}(\eta, \boldsymbol{R}, \boldsymbol{\theta}) \tag{10}$$

$$\begin{aligned} V^{+}(1, \boldsymbol{\rho}, \boldsymbol{\theta}) &= E(\eta, \boldsymbol{R}, \boldsymbol{\theta}) - [T^{+}(\eta, \boldsymbol{R}, \boldsymbol{\theta}) + \varepsilon_i(\eta, \boldsymbol{R}, \boldsymbol{\theta})] \\ &\equiv V^{+}(\eta, \boldsymbol{R}, \boldsymbol{\theta}). \end{aligned} \tag{11}$$

A scaling parameter η^{+} for the cation can be calculated with the knowledge of $\boldsymbol{\rho}^{+}(=\boldsymbol{R})$ and substitution of Eqs. (10) and (11) into an equation for a cation similar to Eq. (4). Scaled energies for the cation, similar to those of Eqs. (5), (6), and (7), can readily be derived using η^{+} and Eqs. (10) and (11). The scaled ionization energy $I_i(\eta^{+}, \eta)$ can then be obtained by using the scaled energies of both the neutral and the cation as in Eq. (12):

$$I_i(\eta^{+}, \eta) = E_i^{+}(\eta^{+}, \boldsymbol{R}^{+}, \boldsymbol{\theta}) - E_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}) \tag{12a}$$

$$\begin{aligned} &= (\eta^{+} - 1) \cdot [\eta^{+} \cdot T(\eta, \boldsymbol{R}, \boldsymbol{\theta}) + E(\eta, \boldsymbol{R}, \boldsymbol{\theta})] \\ &\quad - \eta^{+} \cdot (\eta^{+} - 1) \cdot t_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}) + \varepsilon_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}). \end{aligned} \tag{12b}$$

Equation (12b) indicates that the scaled ionization energy can be calculated using only quantities available from the calculations of the neutral molecule. It is not necessary to carry out any Hartree–Fock calculation for the cation. It is, however, necessary to do some Hartree–Fock calculations at different bond distances for the neutral molecule to find η and η^{+} in Eq. (4), if the derivatives of V, T, V^{+} and T^{+} are calculated numerically.

If Eq. (8) and an equation for the cation similar to it are substituted in Eq. (12a) we have an alternative expression for $I_i(\eta^{+}, \eta)$:

$$\begin{aligned} I_i(\eta^{+}, \eta) &= t_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}) - [T^{+}(\eta^{+}, \boldsymbol{R}^{+}, \boldsymbol{\theta}) - T^{+}(\eta, \boldsymbol{R}, \boldsymbol{\theta})] \\ &\quad - \sum_{l} \left[\rho_l^{+} \cdot \frac{\partial E^{+}(\eta^{+}, \boldsymbol{R}^{+}, \boldsymbol{\theta})}{\partial \rho_l^{+}} - \rho_l \cdot \frac{\partial E(\eta, \boldsymbol{R}, \boldsymbol{\theta})}{\partial \rho_l} \right]. \end{aligned} \tag{13}$$

The right-hand side of Eq. (13) consists of three terms: the first is the kinetic energy of the ith molecular orbital, the second is a kinetic relaxation term (ΔKR), and the third is the net work (ΔW) exerted before and after ionization [10]. Equation (13) has an interpretative value of the ionization energy $I_i(\eta^{+}, \eta)$. The kinetic energy of molecular orbitals has been investigated, which has furnished a set of information on the electronic structure [11-13]. The kinetic relaxation, as mentioned in the previous work [6], assumes a negative value ($\Delta KR < 0$) if the electronic cloud expands and a positive value ($\Delta KR > 0$) if it contracts on ionization. The work term provides information on the nature of the molecular orbital from which an electron is removed depending on the value of ΔW. Following the criterion given in the literature [10], the molecular orbital is bonding ($\Delta W < 0$), non-bonding ($\Delta W = 0$) or anti-bonding ($\Delta W > 0$).

The application of Eq. (12) or Eq. (13) needs care. The first is concerned with the geometry of the molecule. Equation (13) does not imply that the geometry of a neutral molecule is the same as that of an equilibrium molecule. If its geometry is that of equilibrium but the virial theorem is not complied with the scaling method changes the magnitude of the bond lengths through Eq. (3). To find the equilibrium geometry that satisfy the virial theorem, we must have $V(1, \boldsymbol{\rho}, \boldsymbol{\theta})$, $T(1, \boldsymbol{\rho}, \boldsymbol{\theta})$, $\partial V(1, \boldsymbol{\rho}, \boldsymbol{\theta})/\partial \rho_l$ and $\partial T(1, \boldsymbol{\rho}, \boldsymbol{\theta})/\partial \rho_l$ at different $\boldsymbol{\rho}$. Then we calculate η (Eq. 4) and the respective value of $\boldsymbol{R}$ (Eq. 3). With these parameters and the respective energies (Eqs. 5-7), the lengths and the scaled energies of the equilibrium bond are obtained by means of an interpolation technique. So the last term on the right-hand side of Eq. (13) vanishes.

The second point to be mentioned is that the geometry of the scaled cation must be identical to the geometry of the scaled neutral molecule, $\boldsymbol{R}^+ = \boldsymbol{R}_{eq}$, if the vertical ionization energies are desired. This is obtained through the unscaled energies of the cation from the scaled energies of the neutral molecule, as shown in Eq. (10). The cations' energies are defined at the bond lengths $\mathbf{R}$ of the neutral molecule and not $\boldsymbol{\rho}$, that is, $\boldsymbol{\rho}^+ = \boldsymbol{R}$. As in the neutral molecule, when $V^+(1, \boldsymbol{\rho}, \boldsymbol{\theta})$, $T^+(1, \boldsymbol{\rho}, \boldsymbol{\theta})$ and its derivatives are known for different values of $\boldsymbol{\rho}^+$, it is possible to obtain a set of η^+ and $\boldsymbol{R}^+$. Since the cation geometry is identical to that of a neutral molecule, it is possible to find the value of η^+ for which $\boldsymbol{R}^+ = \boldsymbol{R}_{eq}$ through an interpolation technique. Vertical ionization energies may then be calculated with Eq. (12b).

The actual calculations needed to obtain vertical ionization energies follow the steps detailed below:

1. Carry out a set of Hartree-Fock calculations at different values for bond lengths ($\boldsymbol{\rho}$).

2. Find $V(1, \boldsymbol{\rho}, \boldsymbol{\theta})$, $T(1, \boldsymbol{\rho}, \boldsymbol{\theta})$ and calculate their first derivatives with respect to $\boldsymbol{\rho}$. Calculate η for any value of $\boldsymbol{\rho}$ from Eq. (4).

3. With the value of η for each $\boldsymbol{\rho}$, determine the values of scaled energies using Eqs. (5)-(7) and Eq. (9).

4. Apply an interpolation technique to determine $\boldsymbol{R}_{eq}$ and the energies at $\boldsymbol{R}_{eq}$.

5. The unscaled cation energies can be obtained with Eqs. (10)-(11). These energies correspond to the cation geometry where $\boldsymbol{\rho}^+ = \boldsymbol{R}$.

6. With unscaled cation energies and the respective derivatives with respect to $\boldsymbol{\rho}^+$, determine η^+ (equation similar to Eq. 4) and $\boldsymbol{R}^+$ (Eq. 3).

7. With the set of η^+ and $\boldsymbol{R}^+$, determine the value of η^+ where $\boldsymbol{R}^+ = \boldsymbol{R}_{eq}$ by interpolation technique.

8. Calculate vertical ionization potential from Eq. (12b).

9. If there is interest in interpretative option (Eq. 13) the following expressions may be used:

$$\Delta \mathrm{KR} = [(\eta^+)^2 - 1] \cdot [T(\eta, \boldsymbol{R}, \boldsymbol{\theta}) - t_i(\eta, \boldsymbol{R}, \boldsymbol{\theta})] \tag{14}$$

$$\begin{aligned} \Delta W = {} & \eta^+[(2 \cdot \eta^+ - 1) \cdot t_i(\eta, \boldsymbol{R}, \boldsymbol{\theta}) + \varepsilon_i(\eta, \boldsymbol{R}, \boldsymbol{\theta})] \\ & - [2 \cdot (\eta^+)^2 - \eta^+ - 1] \cdot T(\eta, \boldsymbol{R}, \boldsymbol{\theta}) - (\eta^+ - 1) \cdot E(\eta, \boldsymbol{R}, \boldsymbol{\theta}). \end{aligned} \tag{15}$$

This procedure is not restricted to vertical ionization potential.

3. Results and discussion

We have applied the procedure described in the preceding section for some diatomic hydrides of the second-row elements. Throughout this work we have used the ab initio SCF-MO method at the HFR level of approximation using Slater-type orbitals. Minimum basis set with Slater and Best atom atomic orbitals were used following the work of Ransil [14]. $\zeta = 1.2$ was used for the hydrogen $1s$ orbital. Since the results of both types of atomic orbitals are very similar, only the data obtained with the Slater orbitals are presented. Table 1 lists the experimental and calculated bond lengths together with scaling parameters η. A theoretical bond length corresponds to the energy minimum of $E(\eta, \boldsymbol{R}, \boldsymbol{\theta})$ in Eq. (5).

Table 2 compares ionization energies calculated by different methods. The value in the second column (IK_{eq}) and the third one (IK_c) are similar in most cases. The effect of scaling for neutral molecule only (Eq. 9) on Koopmans' theorem is small. However, a detailed comparison between the IK_c and IK_{eq} values reveals that the corrections to Koopmans' theorem through Eq. (9) slightly improve ionization energies to the right direction as seen especially in the cases of 3σ and 1π of OH^-.

The ionization energies obtained by the virial theorem (4th column, IVT) are also similar to the corresponding values of IK_{eq} and IK_c with only exception for

Table 1. Experimental (Rex) and calculated equilibrium bond lengths (Req) (atomic units) and scaling parameter (η)

	R_{ex} [a]	R_{eq}	η
LiH	3.0147	3.02859	0.99533
BH	2.3291	2.40872	0.99572
CH^+	2.1370	2.33172	1.00522
OH^-	1.8103[b]	2.04248	0.97827
HF	1.7331	1.81720	0.99160

[a] Experimental data from [20]

[b] Estimated value from [21]

Table 2. Ionization potentials in atomic units

		IK_{ex} [a]	IK_{eq} [b]	IK_c [c]	IVT [d]	IHAM/3 [e]	I_{exp}
LiH	1σ	2.441	2.441	2.455	2.384	—	—
	2σ	0.305	0.304	0.304	0.304	—	—
BH	1σ	7.659	7.658	7.679	7.506	—	—
	2σ	0.640	0.627	0.624	0.625	—	—
	3σ	0.327	0.326	0.328	0.325	—	—
CH^+	1σ	11.965	11.949	11.914	11.698	11.738	—
	2σ	1.273	1.238	1.235	1.236	1.153	—
	3σ	0.887	0.870	0.866	0.866	0.844	—
OH^-	1σ	19.584	19.644	19.880	19.517	19.313	—
	2σ	0.599	0.582	0.629	0.614	0.765	—
	3σ	−0.075	−0.071	−0.033	−0.043	0.228	—
	1π	−0.259	−0.230	−0.166	−0.190	0.078	0.067[f]
HF	1σ	26.121	26.129	26.239	25.787	25.458	25.51[g]
	2σ	1.461	1.447	1.465	1.450	1.457	1.455[h]
	3σ	0.568	0.554	0.567	0.559	0.728	0.731[i]
	1π	0.446	0.447	0.472	0.451	0.618	0.60[i]

[a] Koopmans' ionization potentials obtained using experimental bond lengths
[b] Koopmans' ionization potentials obtained using equilibrium bond lengths
[c] Corrected Koopmans' ionization potentials (Eq. 9)
[d] Ionization potentials obtained by virial theorem (Eq. 12b)
[e] Ham/3 [17] ionization potentials
[f] Experimental electron affinity [22]
[g] Experimental ionization potential [23]
[h] Experimental ionization potential [24]
[i] Experimental ionization potential [25]

1σ orbitals where an improvement of the theoretical values is noticeable. The effect of the scaling is most significant in the inner core orbitals and is negligible for the valence orbitals. Similar observations have been reported for atoms by Tal and Katriel [8]. The ionization energies of the valence electrons may be improved if the inner shells and valence shells are scaled independently, as in the case of the scaled atoms in molecules (SAIM) theory [15, 16]. The IVTs of 1σ and 2σ for HF and OH^- are in good agreement with the experimental values and/or semiempirical HAM/3 values [17]. Agreement is not so good for 3σ and 1π. The agreement between IVT and HAM/3 values is good for all the molecular orbitals in CH^+.

Table 3 shows the magnitude of relaxation introduced in the cation after application of scaling. The value of the total reorganization effect (ΔER) is considerable for inner orbitals. For other orbitals, the kinetic (ΔKR) and potential (ΔVR) relaxations are significant, with the opposite signs that cause the cancellation resulting in the small total relaxation effect.

One interpretation of the process of ionization can be obtained from Eq. (13). The magnitude of kinetic energy of each molecular orbital gives information

Table 3. Energy relaxation introduced in the cation through the virial theorem on removal of an electron from each orbital indicated in column two

		ΔER[a]	ΔKR[b]	ΔVR[c]
LiH	1σ	−0.070176	1.199435	−1.269611
	2σ	0.000104	0.198230	−0.198125
BH	1σ	−0.173227	3.357234	−3.530461
	2σ	0.001020	0.499788	−0.498769
	3σ	−0.003303	0.596257	−0.599559
CH^+	1σ	−0.216334	4.813302	−5.029635
	2σ	0.001093	0.555260	−0.554167
	3σ	−0.000583	0.611179	−0.611762
OH^-	1σ	−0.363789	8.199420	−8.563209
	2σ	−0.014766	2.112288	−2.127053
	3σ	−0.009558	1.727748	−1.737306
	1π	−0.023953	2.435784	−2.459737
HF	1σ	−0.452288	11.059470	−11.511758
	2σ	−0.014678	2.629167	−2.643845
	3σ	−0.008077	2.078366	−2.086443
	1π	−0.021121	2.865169	−2.886291

[a] Total relaxation: $\Delta ER = E^+(\eta^+, \boldsymbol{R}^+, \boldsymbol{\theta}) - E^+(\eta, \boldsymbol{R}, \boldsymbol{\theta})$

[b] Total kinetic relaxation: $\Delta KR = T^+(\eta^+, \boldsymbol{R}^+, \boldsymbol{\theta}) - T^+(\eta, \boldsymbol{R}, \boldsymbol{\theta})$

[c] Total potential relaxation: $\Delta VR = V^+(\eta^+, \boldsymbol{R}^+, \boldsymbol{\theta}) - V^+(\eta, \boldsymbol{R}, \boldsymbol{\theta})$

about whether the molecular orbital is compact or diffuse. Examples can be seen in the isoelectronic molecules (BH, CH^+) and (OH^-, HF) (Table 4). The larger the nuclear charge, the greater is the kinetic energy due to contraction of the electronic cloud.

The positive values for kinetic relaxation (ΔKR) in Table 3 show that formation of the cation is followed by contraction of the electronic cloud. The contraction can also be seen from the fact that $\eta^+ > 1$ for all molecules (Table 4). The greater the localizability of the molecular orbital, the greater is the magnitude of the kinetic relaxation. For 1σ orbitals, the larger the nuclear charge is, the smaller the scaling parameter. The 2σ and 3σ orbitals present an interesting characteristic. From LiH to CH^+, we see a decrease in η^+ of 2σ and 3σ with the increase in nuclear charge. With the presence of π electrons there is an abrupt increase in η^+. π Electrons present the same behavior as 1σ electrons. The η^+ of 1σ's are always larger than those of valence orbitals where $\eta^+ \simeq 1.0$. The t_i values of 1σ's are an order of magnitude greater than those of the valence orbitals. This combination of facts causes a significant improvement on 1σ ionization energies, leaving ionization energies of the valence orbitals nearly unaffected as has already been seen in Table 2.

The work term in Table 4 would provide information about the nature of the chemical bond. The negative quantities of the work term (−ΔW) are listed in Table 4 to allow direct comparison of them with overlap populations [18], which

Table 4. Fragments of the scaled ionization energies, scaling parameter (η^+) and overlap population (OPOP)

		t_i[a]	$-\Delta W$[b]	η^+	OPOP[c]
LiH	1σ	3.565	0.0184	1.12823	0.00074
	2σ	0.394	0.1079	1.01301	0.37751
BH	1σ	10.822	0.0411	1.11155	−0.00072
	2σ	0.773	0.3519	1.01023	0.36756
	3σ	0.894	0.0271	1.01225	−0.03189
CH^+	1σ	16.242	0.2689	1.10592	−0.00048
	2σ	1.367	0.4238	1.00759	0.22070
	3σ	1.240	0.2362	1.00832	0.05887
OH^-	1σ	28.132	−0.4166	1.08425	−0.00042
	2σ	2.693	0.0332	1.01454	0.17614
	3σ	1.640	0.0449	1.01173	−0.05908
	1π	2.477	−0.2308	1.01669	—
HF	1σ	36.885	−0.0384	1.08469	−0.00043
	2σ	3.847	0.2330	1.01365	0.12947
	3σ	2.360	0.2772	1.01064	0.04907
	1π	3.323	−0.0070	1.01478	—

Atomic units are used

[a] Kinetic energy of molecular orbital

[b] Work term

[c] Overlap population

are given in the last column. A positive value for each molecular orbital means bonding and a negative value, anti-bonding. For HF and LiH molecules complete agreement of signs is seen for both the work terms and the overlap populations.

The two different methods predict that for HF the 1σ is antibonding and 2σ, 3σ are bonding. For LiH 1σ and 2σ are bonding. The agreement of signs for the remainder of the molecules between the work terms and overlap populations is not so good as the case of HF and LiH. Pronounced disagreement between the work terms and the overlap populations is seen in CH^+ and OH^-. Use of a large basis set, such as double zeta plus polarization, for these ions would be required for better agreements.

Compliance with the virial theorem does not imply that the wave function remains self-consistent. Some authors [7, 19] have suggested methods of correcting not only the energies but also the LCAO coefficients of the wave functions for atomic and molecular systems. Comparison of the atomic ionization energies calculated by Isihara [7] and Custodio [6] shows no significant improvement. In the molecules the quantity of the wave function seems to be sensitive to the ΔW term, the requirement of the simultaneous compliance with the virial theorem and self-consistency of the wave function is desirable.

In conclusion, it is shown that imposition of the virial theorem for both neutral and cation within the framework of Koopmans' theorem (Eq. 13) significantly improves theoretical ionization energies of the innermost molecular orbitals, while the effect of the virial theorem is negligible for outermost orbitals. The ionization energy of *i*th molecular orbital can be broken down into three different terms (Eq. 13). The nature of the *i*th molecular orbital can be discussed with reference to the magnitude and signs of these terms.

Acknowledgements. The authors wish to thank Dr Francisco M. Fernandez (INIFTA) for kind suggestions. The services and computer time made available by the computer center of the Universidade Estadual de Campinas (UNICAMP) are acknowledged. We are indebted to the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support.

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