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The virial theorem as an entail for Koopmans' theorem in atomic calculations

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The "frozen" approximation in the Koopmans' theorem suggests that the virial theorem is not obeyed. By imposing the virial theorem to Koopmans' theorem, we observe that the ionization potential of an atomic orbital is directly related to the respective kinetic energy and that the virial theorem introduces some reorganization effect on the electronic cloud. The quantity of reorganization introduced is not hazard, depending on the type of atom as well as the atomic orbital.

Key words: Virial theorem—Koopmans' theorem—relaxation—kinetic energy—atoms

The Koopmans' theorem [1] is frequently used to predict or to interpret photoelectronic spectra. This theorem states that if an electron is removed from an atomic or molecular orbital and it stays unaltered ("frozen" orbitals) after ionization, the orbital energy will be equal to the negative of the ionization energy:

$$E_1 - E_1^+ = -I_i = \varepsilon_i \tag{1}$$

where: E_1 and E_1^+ are the total energies of neutral atom or molecule and ionized one respectively, I_i the ionization energy and ε_i the respective orbital energy. The fact that the theorem does not regard the effects of reorganization and correlation are frequently criticized [2]. Some mathematical methods have been employed to correct these deficiences [3, 4].

Another aspect that was not observed is that Koopmans' theorem does not obey the virial theorem [5]. A necessary condition for a wave function to be considered a satisfactory one is that it obeys the virial theorem. An exact wave function obeys this theorem and consequently the equilibrium between kinetic and potential energies is maintained. So, when we remove one electron and maintain the oribitals "frozen", we are automatically violating the virial theorem. In this work we impose the virial theorem on the Koopmans' one and evaluate its consequences. Only atoms will be treated here.

Considering that the kinetic energy operator is a monoelectronic one, we can write, in the Hartree–Fock approximation, that the energy of an atom obeying the virial theorem is:

$$E_1 = -T_1 = -\sum_{i}^{\substack{\text{Occ.}\\ \text{orb.}}} t_i \tag{2}$$

$$-T_1 = -t_i - T_1^+ \tag{3}$$

where: T_1 is the total kinetic energy of an atom, T_1^+ is the kinetic energy of the "frozen" cation and t_i the kinetic energy of the ith atomic orbital.

For the "frozen" cation the Eq. 2 does not hold. So we cannot say that the Eq. 1 is satisfied when we substitute the total atomic energies by their respective total kinetic ones. To incorporate the virial theorem for cations, we use the scaling process proposed by Löwdin [5]. So:

$$E_\eta^+ = -T_\eta^+ = -\eta^2 \cdot T_1^+ \tag{4}$$

where: E_η^+ and T_η^+ are the total energy and the total kinetic energy for the cation, respectively obeying the virial theorem, η is the scaling parameter of the wave function and is given by:

$$\eta = -V_1^+/(2.T_1^+) \tag{5}$$

where: V_1^+ and T_1^+ are the potential and kinetic energies of the cation without scaling. The effect of the scaling parameter is understood as representing an expansion (if $\eta < 1$) or a contraction (if $\eta > 1$) of the wave function until the equilibrium between kinetic and potential energies is reestablished. Hence, when we use Eq. 4 we are automatically introducing some effect of electronic reorganization into atomic systems. In this manner, combining Eq. 3, Eq. 4 and Eq. 1, we have that the ionization energy will be given by:

$$I_i = t_i - (T_\eta^+ - T_1^+)_i. \tag{6}$$

In this way, after the introduction of the virial theorem to Koopmans' theorem we have that the atomic orbital ionization potential is directly related with the respective kinetic energy. The last term in Eq. 6 represents a kinetic relaxation (ΔKR). This must not be confused with the total relaxation, that is:

$$\Delta\text{ER} = -E_\eta^+ + E_1^+ \tag{7}$$

which includes not only the kinetic but also the potential relaxation.

Eq. 6 represents the calculation of the ionization energy of an electron in any atomic orbital. If we want to calculate the successive ionization energies we must use the equation:

$$I^n = \sum_{l=1}^{n} \{\eta^2_{(l-1)} \cdot t_{k_l} - T_1^{(l)} \cdot \{\eta^2_{(l)} - \eta^2_{(l-1)}\}\}, \tag{8}$$

where k_l indicates the atomic orbital of where we are removing the lth electron and $T_1^{(l)}$ is the total kinetic energy without scaling of the ion with charge (l).

In this paper, we performed a set of calculations for some atoms of the periodic table. We use the MCHF77 (Multi-Configuration Hartree-Fock) program [6] executing all the calculations with only the configuration of the ground state for atoms and ions. Table 1 shows the ionization potential calculated with Eq. 6; those obtained with the Koopmans' approximation; the experimental one; those obtained by the so-called ΔSCF method; the total relaxation introduced by the virial theorem; the respective kinetic relaxation and the scaling parameter for the cations.

The results show us that the ionization potentials obtained by the Koopmans' theorem are always greater than the experimental one. The introduction of the virial theorem diminish the values of these potentials, approaching more to the experimental values. The results obtained by ΔSCF method, meanwhile are smaller than the experimental ones. These last calculation completely introduce the effect of relaxation on the electronic cloud and the results are always smaller than the experimental because there is no consideration of the effect of correlation. But, in the Hartree-Fock approximation and more specifically in the Koopmans' method, we observe that the virial theorem in some cases introduces a considerable correction to the ionization potential. The absolute values of the total relaxation show this. We can also see that the effects of kinetic relaxation are considerably greater than the total one. When we scale the cation's wave function, this tends to contract the electronic cloud (see the scaling parameter in Table 1) and a contraction implies an increase in the magnitude of the kinetic energy. But, the contraction considerably diminishes the magnitude of the potential energy too. So, we observe a great variation in the values of kinetic and potential relaxations, but in opposite direction. The final result is a cancellation of great part of these two relaxations and a considerably small total relaxation effect.

In order to have a better idea of the magnitude of the reorganization effect introduced by the virial theorem on Koopmans' theorem, we correlate the quantitative percentage of relaxation introduced by the virial theorem with the atomic number. Fig. 1 shows that the relaxation percentage for valence electrons increases with the increase of atomic number. When the valence shell is completely filled and electrons are put in another shell, the effect of relaxation introduced by the removal of an electron in the filled shell tends to diminish with the increase of the atomic number. Electrons in the same level n present different relaxation effects depending on the type of the atomic orbital. In general, the p orbitals are more sensitive than the s orbitals. The presence of an electron in an outer level produces alterations in the relaxation originated from the removal of an electron in inner shells.

Table 1. Ionization potentials (in a.u.), relaxation terms (in a.u.) and scaling parameter

Atoms and atomic orbitals		IVT^a	IK^a	IEXP^a_*	$\Delta\mathrm{SCF}^a$	$\Delta\mathrm{ER}^b$	$\Delta\mathrm{KR}^c$	η
Li	1s	2.294	2.478	2.021		0.084	1.218	1.148
	2s	0.196	0.196	0.198	0.196	0.000	0.012	1.001
Be	1s	4.597	4.732	4.079		0.135	2.188	1.132
	2s	0.309	0.309	0.342	0.296	0.001	0.192	1.007
B	1s	7.503	7.695	6.909		0.193	3.430	1.119
	2s	0.492	0.495			0.002	0.466	1.010
	2p	0.308	0.310	0.305	0.291	0.002	0.438	1.011
C	1s	11.081	11.338	10.474		0.257	4.972	1.109
	2s	0.707	0.712			0.005	0.839	1.012
	2p	0.402	0.407	0.415	0.367	0.005	0.828	1.011
N	1s	15.340	15.666	14.664		0.327	6.808	1.101
	2s	0.956	0.964			0.008	1.309	1.012
	2p	0.500	0.509	0.533	0.449	0.008	1.323	1.012
O	1s	20.281	20.681	19.552		0.400	8.933	1.094
	2s	1.238	1.250	0.882		0.012	1.877	1.013
	2p	0.604	0.616	0.500	0.536	0.013	1.924	1.013
F	1s	25.907	26.383	25.211		0.475	11.348	1.088
	2s	1.556	1.572	1.139		0.017	2.543	1.013
	2p	0.712	0.730	0.639	0.629	0.018	2.628	1.014
Ne	1s	32.219	32.772	31.863		0.554	14.050	1.100
	2s	1.908	1.930	1.654		0.022	3.305	1.013
	2p	0.827	0.850	0.794		0.023	3.437	1.014
Na	1s	39.888	40.478	39.397		0.591	16.388	1.075
	2s	2.770	2.797	2.315		0.026	4.072	1.013
Na	2p	1.487	1.518	1.139		0.031	4.405	1.014
	3s	0.182	0.182	0.187		0.000	0.085	1.000
Mg	1s	48.403	49.032	47.960		0.629	18.872	1.069
	2s	3.735	3.768	3.271		0.032	5.008	1.013
	2p	2.243	2.282	1.911		0.039	5.508	1.014
	3s	0.253	0.253	0.279		0.000	0.283	1.001
Al	1s	57.838	58.501	57.332		0.663	21.426	1.064
	2s	4.872	4.911	4.337		0.039	6.012	1.013
	2p	3.171	3.218	2.720		0.047	6.685	1.014
	3s	0.393	0.393			0.000	0.543	1.001
	3p	0.210	0.210	0.220		0.000	0.361	1.001
Si	1s	68.121	68.819	67.585		0.698	24.124	1.056
	2s	6.117	6.163	5.476		0.046	7.146	1.013
	2p	4.205	4.262	3.675		0.057	7.992	1.014
	3s	0.543	0.544			0.001	0.848	1.002
	3p	0.278	0.278	0.298		0.000	0.648	1.001

Table 1. continued

Atoms and atomic orbitals		IVT[a]	IK[a]	IEXP[a] *	ΔSCF[a]	ΔER[b]	ΔKR[c]	η
P	1*s*	79.256	79.989	78.978		0.734	26.962	1.056
	2*s*	7.475	7.529	6.946		0.054	8.400	1.013
	2*p*	5.351	5.418	4.998		0.067	9.423	1.014
	3*p*	0.350	0.351	0.386		0.001	0.987	1.001
S	1*s*	91.241	92.011	90.849		0.770	29.940	1.053
	2*s*	8.948	9.010	8.416		0.062	9.773	1.013
	2*p*	6.610	6.688	6.064		0.078	10.976	1.014
	3*s*	0.881	0.883	0.588		0.002	1.595	1.002
	3*p*	0.421	0.426	0.382		0.001	1.377	1.002
Cl	1*s*	104.078	104.884	103.749		0.807	33.059	1.050
	2*s*	10.536	10.608	9.923		0.072	11.261	1.013
	2*p*	7.982	8.072	7.424		0.090	12.650	1.014
	3*s*	1.071	1.073	0.662		0.002	2.038	1.002
	3*p*	0.505	0.506	0.478		0.002	1.816	1.002
Ar	1*s*	117.766	118.610	117.714		0.844	36.317	1.048
	2*s*	12.241	12.322	11.760		0.081	12.862	1.013
	2*p*	9.469	9.572	9.078		0.102	14.469	1.014
	3*s*	1.274	1.277	0.919		0.003	2.529	1.002
	3*p*	0.588	0.591	0.581		0.002	2.281	1.002
K	1*s*	132.666	133.533			0.867	39.363	1.045
	2*s*	14.402	14.490	13.855		0.089	14.262	1.012
	2*p*	11.408	11.519	10.915		0.111	16.062	1.014
	3*s*	1.745	1.749	1.250		0.004	3.069	1.003
	3*p*	0.951	0.954	0.662		0.004	2.893	1.002
	4*s*	0.148	0.148	0.158		0.000	0.117	1.000

[a] Ionization potentials (obtained by: virial theorem (IVT); Koopmans' approximation (IK), experimental data (IEXP) and ΔSCF method)

[b] Total relaxation (ΔER)

[c] Kinetic relaxation (ΔKR)

* Experimental data from Ref. [12]

Contrasting with the virial theorem we have the technique of adjusting the Koopmans' ionization potentials by a factor of 0.92 [7]. This empirical adjustment has been employed with some success for molecules containing first-row atoms [8]. For atoms only, we could observe that the adjusted ionization potentials with this factor were generally in slightly better agreement with the experimental one than that obtained by the virial theorem. Statistically the difference between the two methods was very small. Correlation coefficients near 1.0 of the calculated ionization potentials with the experimental one were identical in both cases. The smaller deviation of the ionization potentials obtained with the factor 0.92 can be explained by the fact that the virial theorem introduces only some relaxation in the wave function, while the correction introduced by the factor tries to

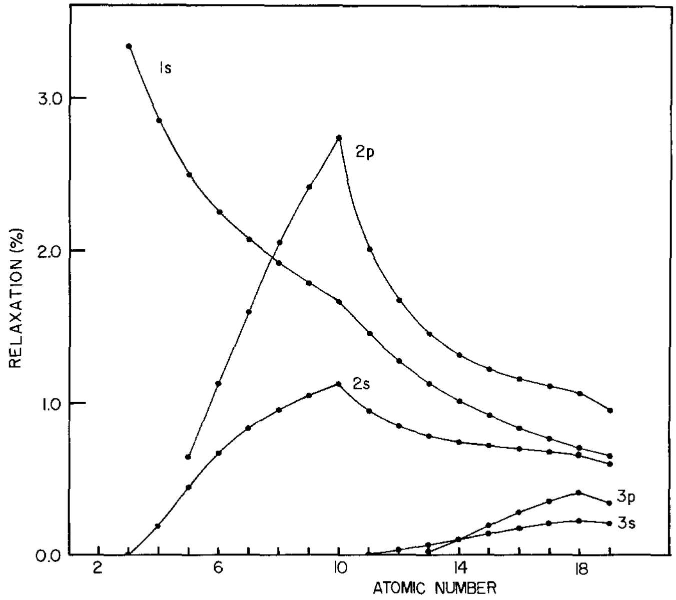

Fig. 1. Diagram of the quantitative percentage of relaxation introduced by the virial theorem in Koopmans' theorem - *versus* - the atomic number

compensate the opposite effects of relaxation and correlation. The great advantage of the application of the virial theorem over the correction is that mathematically it is a rigorous method that searches for reestablishing the equilibrium between the kinetic and potential energies.

Table 2. Successive ionization potentials[a] (in a.u.) for Argon and Oxygen and relaxation percent (% rel.) introduced by the virial theorem in the Koopmans' theorem

Argon	1°	2°	3°	4°	5°	6°	7°	8°
IEXP*	0.579	1.015	1.503	2.197	2.756	3.355	4.557	5.272
IVT	0.588	1.172	1.750	2.324	2.892	3.454	4.694	5.927
IK	0.591	1.182	1.773	2.364	2.955	3.546	4.823	6.101
% rel.	0.453	0.866	1.280	1.715	2.148	2.592	2.684	2.862
Oxygen	**1°**	**2°**	**3°**	**4°**	**5°**	**6°**	**7°**	
IEXP*	0.500	1.290	2.017	2.844	4.185	5.075	27.163	
IVT	0.604	1.176	1.722	2.235	3.344	4.408	22.251	
IK	0.616	1.232	1.849	2.465	3.715	4.966	25.646	
% rel.	2.045	4.561	6.822	9.321	9.991	11.227	13.240	

* Experimental data from Ref. [13].

[a] Ionization potentials obtained by: experimental data (IEXP), virial theorem (IVT) and Koopmans' approximation (IK)

Calculation of consecutive ionization potentials of Ar and O can be observed in Table 2. The results show us that the greater the number of electrons ionized the greater the relaxation introduced by the virial theorem.

In conclusion, we can say that the virial theorem introduces some reorganization effect to Koopmans' theorem. The quantity of relaxation introduced is not hazard, it depends on the type of atom as well as the atomic orbital. An important aspect is that with the aid of the virial theorem we are able to establish some correlation between the atomic orbital kinetic energies, that is an additive energy and the ionization potentials which are observable. In this way we can say that the kinetic energy of atomic orbitals is not similar to the respective ionization energy because of the presence of the kinetic relaxation effect. With the extrapolation of this idea for molecules we believe that we will be able to explain the differences between correlation diagrams made to explain Walsh's rule [9], using canonical [10] and kinetic energy of molecular orbitals [11]. This will be the subject of a future study.

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