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Ab initio Calculations of Core Electron Binding Energies and Shifts in Halomethanes

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Ab initio LCAO MO SCF calculations have been carried out to predict core electron binding energies and shifts in fluoro- and chloro-methanes. The quality of the calculations ranges from a better than double zeta basis set to minimal STO (3 G) basis set. Predictions of binding energies and shifts are made using Koopmans' theorem, hole state calculations and equivalent cores calculations. Using a flexible basis set there is very little difference in the prediction of shifts by these three methods but for minimal basis set calculations the equivalent cores calculations give the best results.

Key words: Core holes – Equivalent cores – Koopmans' theorem – ESCA shifts.

1. Introduction

The accurate measurement of molecular core binding energies using ESCA has stimulated an interest in non-empirical calculations of shifts in core electron binding energies [1, 2]. Three approaches have commonly been used within the Hartree Fock formalism.

1. *Koopmans' Theorem* [3] which equates binding energies to the negative of computed orbital energies.
2. *Hole States*-binding energies are computed as energy differences between the neutral molecule and hole states formed by the removal of core electrons [4].
3. *Equivalent Cores Method*-Shifts in core binding energies are computed from heats of reaction for the isodesmic processes involved in the thermodynamic equivalent cores model [5, 6].

Implicit in all of these approaches is the neglect (or assumed self cancellation) of correlation energy changes. For core levels, however, correlation energy corrections to core electron binding energy shifts are essentially atomic in nature (since core orbitals are so localized) and it seems clear both from the success of these three models and from direct calculations [7] that correlation energy corrections are essentially constant for a given core level.

Koopmans' theorem predictions of shifts are expected to be basis set dependent and even for a large basis set at the Hartree Fock limit electronic relaxation is neglected. Thus, unless the electronic relaxation energy is constant or varies in a regular manner for a particular series of molecules then Koopmans' theorem is not expected to yield a quantitative description of shifts in core binding energies. The core hole state calculations take into account electronic relaxation but may give convergence difficulties in the SCF procedure. When there is more than one equivalent centre in a molecule the question of localized versus non-localized hole states presents computational problems. The available evidence from direct calculations [7], from the success of the equivalent cores model (implicit in which is the concept of localized core holes) and the observation of certain shake-up transitions (formally forbidden if the hole state is delocalized) [8] is compelling in favour of the description of core hole states in such systems as being localized on the time scale of the ESCA experiment. However the theoretical treatment of such states is much more difficult than for delocalized hole states. In investigating the effect of electronic relaxation as a function of electronic environment and basis set therefore it is convenient to avoid such problems by considering a series of molecules where there is a unique hole state. The equivalent cores method depends on the energy of core exchange (in a series of isodesmic reactions) remaining constant and the calculated value for this energy may well depend on the basis set used.

While independent applications of these three approaches to the discussion of core binding energy shifts have been made (cf. Refs. [1, 2, 4, 6, 9]) no detailed comparisons of these methods and their dependence on basis sets have been carried out. It is the purpose of this paper to investigate in detail each of these methods to obtain information on their basis set dependencies, relaxation energies and the validity of the constancy of the energy of core exchange as a function of electronic environment. The systems studied are fluoro- and chloromethanes for which the experimental data are well documented [1, 10, 11].

2. Calculations

Ab initio LCAO MO SCF calculations on the molecules $CH_{4-n}F_n (n=0-4)$, CH_3Cl and CH_2Cl_2 together with the isoelectronic series $NH_{4-n}F_n^+$, NH_3Cl^+ and $NH_2Cl_2^+$ were carried out using a better than double zeta basis set of optimised gaussian functions [12]. These consisted of 4*s* contracted to 3*s* for hydrogen (scale factor 1.2) and 9*s*, 5*p* contracted to 5*s*, 3*p* for carbon, nitrogen and fluorine. A 12*s*, 9*p* basis set was used for chlorine [13] and this was contracted to 7*s*, 5*p* according to the principles outlined by Dunning [12]. For ease of reference this basis set will be referred to later as "the large basis set". These calculations, except for CH_2Cl_2 and $\overset{+}{N}H_2Cl_2$ were performed using the IBMOL V LCAO MO SCF programme [14], all other calculations reported here were performed using the ATMOL group of programmes [15]. The programmes were implemented on an IBM 360/195.

Calculations on the series $CH_{4-n}F_n$, $NH_{4-n}F_n^+$ and $^*CH_{4-n}F_n^+$ (where * indicates a vacancy in the C_{1s} shell) were carried out using the following smaller basis sets.

1. The core orbitals were represented by four contracted gaussians and the valence orbitals, including H_{1s} (scale factor 1.2) were represented by four gaussian functions contracted to groups of 3 and 1 thus allowing a more flexible description of the valence orbitals. (STO 4.31 G basis set).

2. Each orbital was represented by three contracted gaussian functions with a 1.2 scale factor for the H_{1s} (STO 3 G basis set).

The exponents and coefficients used for these two basis sets were those obtained by Stewart [16], from a least squares fit of gaussian functions to Clementi's STO SCF atomic orbitals [17].

3. Results

Koopmans' Theorem

The Koopmans' theorem prediction of the binding energies and the shifts are shown in Table 1 together with the experimental values. The accuracy with which shifts in C_{1s} core binding energies are predicted, as expected, increases with increased flexibility of the basis set (Fig. 1), but even the large basis set overestimates the shift between CH_4 and CF_4 by ~22%. Koopmans' theorem neglects electronic relaxation on ionization, however this is not a reasonable assumption. Gelius and Siegbahn [18] have divided the molecular electronic reorganization energy from atom A, $E_A^{reorg}(mol)$, into two terms

$$E_A^{reorg}(mol) = E_A^{contr} + E_A^{flow}$$

where the first term is the reorganization energy gained by the contraction of the local charge distribution around nucleus A and is essentially atomic. The second term represents the redistribution of electron density in the remainder of the molecule. Using the differences between the calculated binding energies using the negative of the Hartree Fock orbital energies (Koopmans' theorem) and the differences in the total energies of the atom and ion Gelius and Siegbahn have estimated the atomic reorganization energy for the 1*s* ionization of carbon to be 13.7 eV [18]. This value accounts for most of the difference between the experimental binding energies and the Koopmans' theorem values

Table 1. Koopmans' theorem predictions

Molecule	3 G		4.31 G		Large basis		Experimental[a]	
	BE	Shift	BE	Shift	BE	Shift	BE	Shift
	C_{1s} Shifts and binding energies (eV)							
CH_4	305.43	0.0	304.35	0.0	304.95	0.0	290.7	0.0
CH_3F	309.64	4.21	307.43	3.08	307.75	2.80	293.5	2.8
CH_2F_2	313.90	8.47	310.82	6.47	310.81	5.86	296.3	5.6
CHF_3	318.25	12.81	314.40	10.05	314.08	9.13	299.0	8.3
CF_4	322.69	17.26	317.96	13.61	317.38	12.43	301.7	11.0
CH_3Cl	—	—	—	—	307.49	2.54	292.3	1.6
CH_2Cl_2	—	—	—	—	309.77	4.82	293.9	3.1
	F_{1s} Shifts and binding energies (eV)							
CH_3F	704.50	0.0	713.24	0.0	714.90	0.0	692.4	0.0
CH_2F_2	705.70	1.20	714.41	1.17	716.13	1.23	693.1	0.7
CHF_3	706.91	2.41	715.60	2.36	717.31	2.41	694.1	1.7
CF_4	708.17	3.67	716.76	3.52	718.46	3.56	695.0	2.6

[a] See Refs. [2, 10, 11].

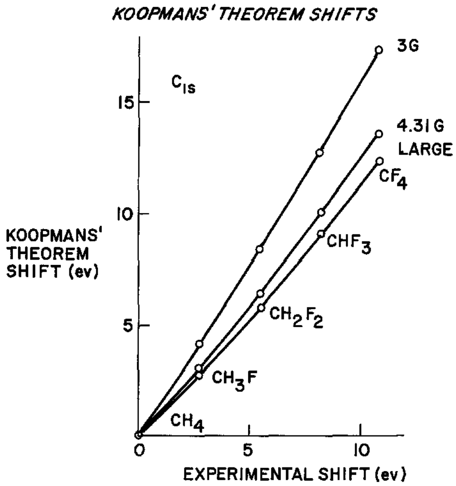

Fig. 1. Plot of Koopmans' theorem shifts (w.r.t. CH_4) versus experimental shifts for the fluoromethanes as a function of basis set

in the cases of the 4.31 G and the large basis set calculations while the differences for the 3 G calculations are slightly larger. The estimate of a reorganization energy of 22.0 (or 22.1 employing a relativistic calculation) [18] for F_{1s} ionization accounts for most of the observed difference in the large basis set calculations but slightly overestimates the difference in the case of the 4.31 G calculations and grossly overestimates the difference in the case of the 3 G calculations. We attribute these differences to the poorer descriptions of the system given by the smaller basis sets. However the fact that with an improved basis set the shifts are well described by Koopmans' theorem suggests that reorganization energy differences contribute to only a minor extent for these closely related molecules. This will be discussed in more detail in a later section.

Hole State Calculations[1]

The binding energy of a core electron e.g. in methane is the energy for the process

$$CH_4 \rightarrow {}^*CH_4^+ + e^- \qquad \Delta E = BE_{CH_4}$$

where * indicates a vacancy in a core level, carbon 1*s* in this case. Since the photoionization process is rapid compared to nuclear motion the core hole states were taken to have geometries identical to the parent molecule and the total energies for 3 G and 4.31 G calculations on the series $CH_{4-n}F_n$ and ${}^*CH_{4-n}F_n^+$ are included in Table 2. The calculated binding energies and shifts

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[1] For the hole states RHF calculations corresponding to the appropriate *locked* configurations have been carried out. There is no absolute guarantee that variational upper bounds to the true total energies for the ions are obtained since the computed hole states are not necessarily orthogonal to all lower energy states of the same symmetry. This could introduce errors of both a systematic and/or non-systematic nature. The results however would indicate that these considerations have not been encountered in this work.

Cf. Gianturco, F. A., Cuidotti, G., Chem. Phys. Letters **9**, 539 (1971).

Table 2. Total energies (eV)

n	$CH_{4-n}F_n$			$*CH_{4-n}F_n^+$		$NH_{4-n}F_n^+$		
	3 G	4.31 G	Large	3 G	4.31 G	3 G	4.31 G	Large
0	− 1078.1863	− 1089.0380	− 1093.4785	− 780.6724	− 796.1041	− 1514.4967	− 1531.2662	− 1537.7923
1	− 3720.4685	− 3766.3545	− 3783.1361	− 3418.3047	− 3470.1125	− 4153.8329	− 4205.5299	− 4224.5316
2	− 6363.0474	− 6443.9813	− 6473.2378	− 6056.0838	− 6144.2386	− 6793.0207	− 6879.8908	− 6911.4577
3	− 9005.7991	− 9121.6151	− 9163.4585	− 8693.8839	− 8818.3430	− 9431.9449	− 9554.1786	− 9598.3631
4	−11648.5597	−11798.8994	−11852.3984	−11331.5514	−11492.2842	−12070.5013	−12228.2038	−12283.9676
		CH_3Cl	−13580.5603				NH_3Cl^+	−14023.0044
		CH_2Cl_2	−26067.4141				$NH_2Cl_2^+$	−26508.2375

Table 3. Hole state calculations

	3 G		4.31 G		Experimental[a]	
	BE	Shift	BE	Shift	BE	Shift
			C_{1s} binding energies and shifts (eV)			
CH_4	297.51	0.0	292.93	0.0	290.7	0.0
CH_3F	302.16	4.65	296.24	3.31	293.5	2.8
CH_2F_2	306.96	9.45	299.76	6.81	296.3	5.6
CHF_3	311.92	14.41	303.27	10.34	299.0	8.3
CF_4	317.01	19.50	306.62	13.69	301.7	11.0

[a] Ref. [11].

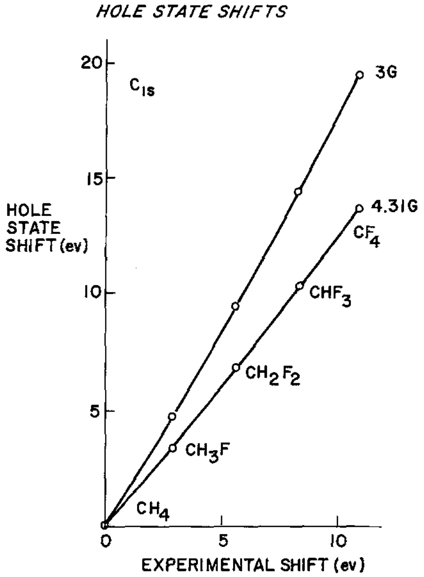

Fig. 2. Plot of hole state shifts (w.r.t. CH_4) versus experimental shifts for the fluoromethanes as a function of basis set

obtained from the difference in energy between the molecule and the core hole states are listed in Table 3 and the shifts are illustrated in Fig. 2. These calculations take into account electronic reorganization on core ionization and give binding energies which are in better agreement with the experimental values than are the Koopmans' theorem energies. However, for the 3 G and 4.31 G calculations the prediction of the shifts is not as good as the Koopmans' prediction, but for a double zeta calculation on the ground states and core hole states of $CH_{4-n}F_n$ ($n=0$ to 3) Brundle, Robin and Basch [19] have shown that the shifts are predicted with about equal accuracy by both methods.

Equivalent Cores Shifts

The equivalent cores method of predicting shifts in core electron binding energies from thermodynamic data was developed by Jolly and Hendrickson [5]. Where thermodynamic data are available this method gives good predictions of shifts [20]. The principle of equivalent cores may be stated: "When a core electron is removed from an atom molecule or ion, the valence electrons adjust as if the nuclear charge of the atom had increased by one unit". Consider, for example, the shift in C_{1s} binding energy between CH_4 and CH_3F.

$$CH_4 \rightarrow {}^*CH_4^+ + e^- \qquad \Delta E = B_{CH_4}, \qquad (1)$$

$$^*CH_4^+ + N^{5+} \rightarrow NH_4^+ + {}^*C^{5+} \qquad \Delta E = \delta_0, \qquad (2)$$

$$(1)+(2) \quad CH_4 + N^{5+} \rightarrow NH_4^+ + {}^*C^{5+} + e^- \qquad \Delta E = B_{CH_4} + \delta_0. \qquad (3)$$

Similarly for CH_3F

$$CH_3F \rightarrow {}^*CH_3F^+ + e^- \qquad \Delta E = B_{CH_3F}\,, \tag{4}$$

$$ {}^*CH_3F^+ + N^{5+} \rightarrow NH_3F^+ + {}^*C^{5+} \qquad \Delta E = \delta_1\,, \tag{5}$$

$$(4)+(5) \quad CH_3F + N^{5+} \rightarrow NH_3F^+ + {}^*C^{5+} + e^- \quad \Delta E = B_{CH_3F} + \delta_1\,. \tag{6}$$

The shift in core binding energies is thus given by

$$(6)-(3) \quad CH_3F + NH_4^+ \rightarrow NH_3F^+ + CH_4 \qquad \Delta E = B_{CH_3F} - B_{CH_4} + (\delta_1 - \delta_0)\,. \tag{7}$$

It is assumed in the equivalent cores approximation that the values δ_0 and δ_1 are small since the species $^*CH_4^+$ and NH_4^+, $^*CH_3F^+$ and NH_3F^+, and $^*C^{5+}$ and N^{5+} are taken to be chemically equivalent. The shift in binding energy is therefore given by the heat of reaction for (7). However, this expression is still valid even if δ_1 and δ_0 are not zero provided that $\delta_1 - \delta_0 = 0$, i.e. provided that the heats of reaction for core exchange are independent of the molecular environment for a particular pair of elements.

The energies for reaction of the type (7) may be calculated from SCF calculations on the individual molecules in their ground states. Semi empirical calculations of the equivalent cores shifts using all valence electron SCF MO calculations have been qualitatively successful [20–22] and *ab initio* minimal Slater basis set calculations have been more successful [6, 9]. It is therefore of interest to determine how much improvement is obtained when an extended basis set is used. Since photoionization is rapid compared with nuclear motion the geometries for the nitrogen cations were taken to be identical with those of the isoelectronic molecules. (This is also convenient on computational grounds since many of the two electron integrals can be retained.)

The total energies required to calculate the equivalent cores shifts in C_{1s} binding energies are shown in Table 2 and the equivalent cores shifts are shown in Table 4 and Fig. 3. The shifts are predicted well even by the smaller basis set calculations and in this respect they show less dependence on the choice of basis set than do the Koopmans' theorem and hole state calculations. For the large basis set calculations the equivalent cores shifts and Koopmans' theorem shifts are closely similar and this near equality is also observed between hole state shifts and Koopmans' theorem shifts when a double zeta basis set is used [19].

Table 4. Equivalent cores shifts (eV)

	3 G	4.31 G	Large	Experimental[a]
CH_4	0.0	0.0	0.0	0.0
CH_3F	2.95	3.05	2.82	2.8
CH_2F_2	6.34	6.31	5.99	5.6
CHF_3	10.16	9.66	9.31	8.3
CF_4	14.37	12.92	12.64	11.0
CH_3Cl			1.77	1.6
CH_2Cl_2			3.39	3.1

[a] Refs. [10] and [11].

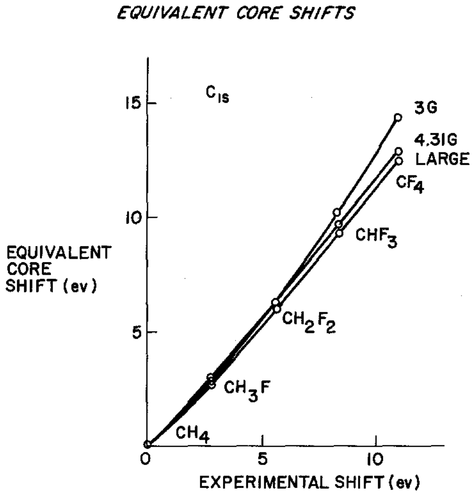

Fig. 3. Plot of equivalent core shifts (w.r.t. CH_4) versus experimental shifts for the fluoromethanes as a function of basis set

It would therefore appear at least in the case of the fluoromethanes that all three methods of calculation tend towards the same results as the flexibility of the basis set increases.

The accuracy with which the equivalent cores method predicts shifts depends on how close the value of $\delta_1 - \delta_0$ is to zero. It is therefore of interest to calculate the values of $\delta_1 - \delta_0$ predicted by these calculations.

$$
\begin{array}{ll}
{}^*CH_{4-n}F_n^+ + N^{5+} \rightarrow NH_{4-n}F_n^+ + {}^*C^{5+} & \Delta E = \delta_n , \\
NH_4^+ + {}^*C^{5+} \rightarrow {}^*CH_4^+ + N^{5+} & \Delta E = -\delta_0 , \\
{}^*CH_{4-n}F_n^+ + \overset{+}{N}H_4 \rightarrow NH_{4-n}F_n^+ + {}^*CH_4^+ & \Delta E = \delta_n - \delta_0 .
\end{array}
$$

Values of $\delta_n - \delta_0$ have been calculated from the 3 G and 4.31 G results (Table 2) and are shown in Table 5. Large deviations from zero occur with the 3 G calculations but the deviations in the case of the 4.31 G calculations are much smaller. It should be noted that the $\delta_n - \delta_0$ values correspond to the difference in binding energy between the hole state and equivalent cores calculations and the deviation of $\delta_n - \delta_0$ from zero actually acts as an improvement to the hole state calculations bringing them nearer to the experimental values. However, the deviation of $\delta_n - \delta_0$ from zero is reduced greatly by the improvement of the basis set and a value of $(\delta_n - \delta_0) = 0$ would mean that the equivalent cores and hole state calculations would predict the same shifts in core binding energies.

An experimental estimate of the value of δ can readily be obtained for free atoms using ionization energy data to estimate the binding energy and comparing this with experimental measurements of the binding energy. Consider the following processes:

(1) 1*s* ionization in a carbon atom

$$C \rightarrow {}^*C^+ + e^- \qquad \Delta E = B_C .$$

Table 5. Calculated values of $\delta_n - \delta_0$

	n	$\delta_n - \delta_0$ (eV) 3 G	4.31 G
CH_4	0	0.0	0.0
CH_3F	1	−1.70	−0.26
CH_2F_2	2	−3.11	−0.49
CHF_3	3	−4.24	−0.67
CF_4	4	−5.13	−0.76

From calculations on $*C^{5+}$ and N^{5+} with corresponding basis sets, values of δ_0 may be obtained from the data given below

Total energies (eV)

	3 G	4.31 G
$*C^{5+}$	− 483.6457	− 486.7477
N^{5+}	−1202.5878	−1212.6748
δ_0	− 13.78	− 9.24

Since in all cases only a single STO is used to describe the cores (being either a linear combination of three or four gaussians) it is clear that δ_0 is very sensitive to basis set. The detailed dependence on basis set will be discussed elsewhere.

(2) Exchange of $*C^{5+}$ core for equivalent N^{5+} core

$$*C^{+} + N^{5+} \rightarrow *C^{5+} + N^{+} \qquad \Delta E = \delta\,.$$

The sum of these reactions gives an estimate of the C_{1s} binding energy which will differ from the experimental value by δ

$$C + N^{5+} \rightarrow *C^{5+} + N^{+} + e^{-} \qquad \Delta E = B_C + \delta\,.$$

The energy of this reaction is the difference in the energy of the processes

$$C \rightarrow *C^{5+} + 5e^{-} \qquad \Delta E_C = \sum_{i=1}^{5} (IP_C)_i$$

$$N^{+} \rightarrow N^{5+} + 4e^{-} \qquad \Delta E_N = \sum_{i=2}^{5} (IP_N)_i\,.$$

Hence

$$B_C + \delta = \Delta E_C - \Delta E_N = \sum_{i=1}^{5} (IP)_c - \sum_{i=2}^{5} (IP)_N$$

Using values of ionization potentials from Moores tables [23] gives

$$B_{C_{1s}} + \delta = 287.6\ \text{eV}$$

From gas phase measurements the 1*s* binding energy of a carbon atom in benzene, i.e. one with approximately zero (CNDO) charge, is 290.4 eV [24]. This gives a value of δ of about −2.8 eV. There will, however, be somewhat different electronic reorganization energies on ionization from a free atom and a neutral atom in a molecule. Similar estimates of core binding energies and δ have been made for a large number of atoms [25]. Shirley has recently made theoretical estimates of energies for core exchange in CH_4 and CH_3F, and found the values of $\delta = 6.0$ and 5.9 eV respectively [26]. The reason for this discrepancy between theory and experiment is uncertain.

Chloromethanes

The Koopmans' theorem predictions, Table 1, overestimate the C_{1s} binding energy shifts and the error is larger than that obtained for CH_3F which has a C_{1s} shift, intermediate between CH_3Cl and CH_2Cl_2. The equivalent cores shifts are, however, in good agreement with the experimental values. We attribute the differing accuracy in the Koopmans' theorem results partly to the difficulty in obtaining fully compatible basis sets for the first and second row elements, and the improvement obtained from the equivalent cores calculations again illustrates the comparative lack of basis set dependency of this method.

4. Conclusion

These results, together with those of Brundle *et al.* [19] indicate that for the halomethanes when using large basis set calculations there is little difference between the shifts in core binding energies predicted by Koopmans' theorem, hole state and equivalent cores calculations. However if a minimal basis set is employed the best estimates of the shift are obtained from the equivalent cores calculations. The graphs (Figs. 1 – 3) illustrates clearly the order of decreasing basis set dependency of the predicted shifts to be:

$$\text{Hole state} > \text{Koopmans'} > \text{Equivalent cores}\,.$$

The results also suggest that for these closely related molecules differences in relaxation energies are small and therefore make only minor contributions to the shifts in binding energies. In this connection it is of interest to pursue the analysis of the relaxation (reorganization) energies as suggested by Gelius and Siegbahn [18]. The dominant contribution is that arising from the local charge distribution (E_A^{contr}) and may be expressed as

$$E_A^{\text{contr}} = k' q_A + l'_A$$

where q_A is the charge on atom A before ionization, k' is a constant (2.5 eV in an atom [18, 27] and l'_A is the reorganization energy due to orbital contraction around a neutral atom in the molecule (13.7 eV for a carbon atom [18]). Estimates of the relaxation energy obtained from differences between binding energies calculated from Koopmans' theorem and hole states are shown in Table 6 together with atomic charges for the 4.31 G basis set calculations. These overall relaxation energies, which include E_A^{flow}, are essentially constant. This is consistent with the tendency for Koopmans' theorem, hole state calculations and equivalent cores calculations to give the same estimates of shifts with flexible basis sets despite the fact that Koopmans' theorem neglects electronic relaxation while the hole states and equivalent cores calculations take it into account.

Table 6. Charges and relaxation energies (4.31 G basis set)

Molecule	Atom	Charge	Relaxation energy (eV) (Koopmans' B.E. − Hole state B.E.)
CH_4	C	−0.875	11.4
	H	+0.219	—
CH_3F	C	−0.281	11.2
	H	+0.226	—
	F	−0.399	—
CH_2F_2	C	+0.373	11.1
	H	+0.251	—
	F	−0.379	—
CHF_3	C	+0.754	11.1
	H	+0.308	—
	F	−0.354	—
CF_4	C	+1.328	11.3
	F	−0.332	—

It is unrealistic to compare directly the atomic relaxation energy data of Gelius and Siegbahn [18] with that calculated for the fluoromethanes because of differences in basis set. However, the prediction of a near constancy of relaxation energies for the fluoromethanes is interesting and from the analysis of Gelius and Siegbahn [18] this would only be expected if the sum of the charge dependent terms in E_A^{contr} and E_A^{flow} was constant. The charge dependent term in E_A^{contr} increases with increasing positive charge on the carbon atom along the series CH_4 to CF_4 and this implies that E_A^{flow} shows a similar charge dependency on the increasing total negative charge on the atoms bonded to carbon such that the sum total remains essentially constant.

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