The extended Koopmans' theorem: Vertical ionization potentials from natural orbital functional theory

Mario Piris, Jon M. Matxain, Xabier Lopez, and Jesus M. Ugalde

Additional information on J. Chem. Phys.

The extended Koopmans' theorem: Vertical ionization potentials from natural orbital functional theory

Mario Piris,[1,2] Jon M. Matxain,[1] Xabier Lopez,[1] and Jesus M. Ugalde[1]

[1]*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), P.K. 1072, 20080 Donostia, Euskadi, Spain*
[2]*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi, Spain*

The Piris natural orbital functional, PNOF5, has been used to predict vertical ionization potentials of a selected set of 30 organic and inorganic spin-compensated molecules by means of the extended Koopmans' theorem. Electron affinities of 10 selected radicals have also been estimated as the inverse of the ionization potentials of the anionic species, calculated at the experimental geometries of the neutral radicals. The basis set limit effects have been assessed by inspecting the data obtained for the Dunning's basis set series cc-pVXZ and aug-cc-pVXZ (X = D, T, Q, 5). The performance of the PNOF5 is established by carrying out a statistical analysis of the mean absolute errors (MAEs) with respect to the experiment values. The calculated PNOF5 ionization potentials and electron affinities agree satisfactorily with the corresponding experimental data, with MAEs smaller than 0.5 eV. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4709769]

I. INTRODUCTION

Koopmans' theorem (KT) (Ref. 1) provides the theoretical justification for interpreting canonical Hartree-Fock (HF) orbital energies as ionization potentials (IPs). The KT states that given an N-electron single determinant wavefunction with occupied spin-orbital energies ε_i, the IP for removing an electron from spin-orbital ϕ_i is just $-\varepsilon_i$. This approximation neglects evidently relaxation of the spin-orbitals in the $(N-1)$-state and consequently, tends to produce too positive IPs. In addition, the approximation of the wavefunction by a single determinant leads to errors associated with the correlation effects that tend to cancel in part the relaxation error. Because of this fortuitous cancellation of the correlation and relaxation errors, the occupied HF orbital energies commonly provide a reasonable first description of vertical IPs.

A procedure for calculating IPs from correlated wavefunctions is given by the extended Koopmans' theorem (EKT), developed independently by Day *et al.*,[2–4] and by Morrell *et al.*[5] Like KT, the EKT keeps the distinctive advantage of describing the electron detachment in terms of one-electron concepts in one calculation without resorting to multiple energy-difference calculations. Theoretical[6] and numerical[7–11] investigations have demonstrated that EKT is exact for the lowest IP and capable of yielding accurate higher IPs. A theorem that provides a sufficient condition for the validity of the EKT has been also formulated.[12] Efficient approaches to the estimation of IPs of atoms and molecules have likewise been derived from the EKT.[13] Accordingly, the assessment of IPs by means of the EKT constitutes a useful test for a correlated method.

The natural orbital functional (NOF) theory[14–18] has emerged in recent years[19–65] as an alternative method to conventional *ab initio* approaches and density functional theory for considering the electronic correlation. A major advantage of the NOF method is that the kinetic energy and the exchange energy are explicitly defined using the one-particle reduced density matrix (1-RDM) and do not require the construction of a functional. The unknown functional in a 1-RDM theory only needs to incorporate electron correlation. The NOF theory has been reviewed in a recent paper[66] where further details may be found.

One route[67,68] to the construction of approximate 1-RDM functional involves the employment of a reconstruction functional $\mathbf{D}[\Gamma]$ based on the cumulant expansion[69,70] of the two-particle reduced density matrix (2-RDM). In this vein, NOF theory can also be understood as a 2-RDM theory with connections to the parametric 2-RDM methods.[71,72] We shall use the reconstruction functional proposed in Ref. 73, in which the two-particle cumulant is explicitly reconstructed in terms of two matrices, $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$, $\mathbf{n}$ being the set of the occupation numbers. The $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$ matrices satisfy known necessary N-representability conditions and sum rules of the 2-RDM, or equivalently, of the functional. Moreover, precise constraints that the two-particle cumulant matrix must fulfill in order to conserve the expectation values of the total spin and its projection have been formulated and implemented for the matrices $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$.[53] Appropriate forms of the matrices $\Delta(\mathbf{n})$ and $\Pi(\mathbf{n})$ led to different implementations of NOF, known in the literature as PNOFi (i = 1–5).[49,55–57,73] A detailed account of these functionals can be found elsewhere.[74]

The aim of the present paper is to apply PNOF5 (Refs. 44, 57, 75) to the determination of IPs of selected spin-compensated molecules. This is not the first NOF study of IPs via the EKT in molecular systems. Pernal and Cioslowski,[76] as well as, Leiva and Piris,[77] have successfully determined the IPs of selected molecules using NOFs proposed in Refs. 78, 79, and 73 respectively. Farnum and Mazziotti have extracted ionization energies via the 2-RDM by the EKT as well.[80] Moreover, the PNOF2 energy[49] plus the extended Koopmans' IP calculations of the neutral helium dimer have

been successfully used for computing the ground-state energies of radical helium dimer (He_2^+) as a function of the internuclear distance.[52] PNOF5 is expected to be superior because it carries the D, Q, and G positivity necessary N-representability conditions of the 2-RDM (Ref. [81]) through the variational energy minimization process. Additionally, it accounts for the essential orbital interactions for a reliable description of the static correlation effects.[44,57]

On the other hand, electron affinities (EAs) are considerably more difficult to calculate than IPs via both KT and EKT. HF calculations almost always give positive orbital energies for all the virtual orbitals, so KT is unable to predict many stable negative ions. Conversely, PNOF5 involves properly all orbitals connecting them to one-particle energies, the Lagrangian multipliers, and fractional occupation numbers.[44,57] At present, EKT provides an overall unsatisfactory description of the EAs. A goal of the present paper is also to assess the estimation of the EAs of selected radicals as the inverse of the IP of the corresponding anionic species, calculated at the experimental geometry of the neutral radicals.

This article is organized as follows. We start in Sec. II with the basic concepts and notations related to PNOF5 and EKT. Section III is dedicated to present our results obtained for the lowest vertical IPs on a set of 30 organic and inorganic molecules, and the EAs calculated for a selected set of 10 radical species. The performance of the PNOF5 is established by carrying out a statistical analysis of the IP mean absolute errors (MAEs) with respect to the experiment values.

II. THEORY

We briefly describe here the theoretical framework of our approach. A more detailed description of the PNOF5 can be found in Ref. [57].

Assuming a real set of natural orbitals, the PNOF5 energy for a singlet state of an N-electron molecule can be cast as

$$E = \sum_{p=1}^{N}[n_p(2H_{pp} + J_{pp}) - \sqrt{n_{\tilde{p}}n_p}K_{p\tilde{p}}]$$
$$+ \sum_{p,q=1}^{N}{}'' n_q n_p(2J_{pq} - K_{pq}), \qquad (1)$$

where p denotes the spatial natural orbital and n_p its occupation. H_{pp} is the pth matrix element of the kinetic energy and nuclear attraction operators, whereas $J_{pq} = \langle pq|pq\rangle$ and $K_{pq} = \langle pq|qp\rangle$ are the usual Coulomb and exchange integrals, respectively. The $\tilde{p}$-state defines the coupled natural orbital to the orbital p, namely, $\tilde{p} = N - p + 1$, N being the number of particles in the system. In accordance to this assumption, all occupancies vanish for $p > N$. The double prime in Eq. (1) indicates that both the $q = p$ term and the coupled one-particle state terms $p = \tilde{p}$ are omitted from the last summation.

It is worth noting that through the variational minimization of the energy with respect to the natural orbitals and their occupation numbers, we determine the pairs of coupled orbitals $(p, \tilde{p})$, which yield the minimum energy for the functional of Eq. (1). The actual p and $\tilde{p}$ orbitals paired are not constrained to remain fixed along the orbital optimization pro-

cess. Consequently, the pairing scheme of the orbitals is allowed to vary along the optimization process until the most favorable orbital interactions are found.

Additionally, the bounds that stem from imposing the N-representability D and Q positivity necessary conditions of the 2-RDM, imply that the occupation of the $\tilde{p}$ level must coincide with that of the hole of its coupled state p, namely,

$$n_{\tilde{p}} = h_p, \qquad n_{\tilde{p}} + n_p = 1, \qquad (2)$$

where h_p denotes the hole, $1 - n_p$, associated to the spatial orbital p.

The solution in the NOF theory is established by optimizing the energy functional with respect to the occupation numbers $\{n_p\}$ and to the natural orbitals $\{\varphi_p(\mathbf{r})\}$, separately. In the present study, the iterative diagonalization procedure introduced by Piris and Ugalde[54] has been employed. Notice that PNOF5 allows constraint-free minimization with respect to the occupation numbers, which yields substantial savings of computational time.[57] Therefore, one has to minimize the energy (1) with respect to the real orbitals $\{\varphi_p(\mathbf{r})\}$ under the orthonormality constraints. Introducing the set of symmetric Lagrange multipliers $\{\lambda_{qp}\}$, the functional whose extremum we seek is given by

$$\Omega = E - 2\sum_{pq}\lambda_{qp}[\langle\varphi_p|\varphi_q\rangle - \delta_{pq}]. \qquad (3)$$

The Euler equations for functions $\{\varphi_p(\mathbf{r})\}$ are

$$\frac{\delta\Omega}{\delta\varphi_p} = 4\left[n_p\widehat{V}_p\varphi_p(\mathbf{r_1}) - \sum_q\lambda_{qp}\varphi_q(\mathbf{r_1})\right] = 0, \qquad (4)$$

where the one-particle operator $\widehat{V}_p$ is given by

$$\widehat{V}_p(1) = \widehat{H}(1) + \hat{J}_p(1) - \sqrt{\frac{h_p}{n_p}}\hat{K}_{\tilde{p}}(1)$$
$$+ \sum_{q=1}^{N}{}'' n_q[2\hat{J}_q(1) - \hat{K}_q(1)], \qquad (5)$$

$$\hat{J}_q(1) = \langle\varphi_q|r_{12}^{-1}|\varphi_q\rangle, \; \hat{K}_q(1) = \langle\varphi_q|r_{12}^{-1}\widehat{P}_{12}|\varphi_q\rangle.$$

Here, the $\widehat{P}_{12}$ operator permutes electrons 1 and 2, and the integration is carried out only over the coordinates of 2.

It is worth noting that PNOF is not invariant with respect to a unitary transformation of the orbitals,[66] *ergo* Eq. (4) for the optimum orbitals is actually the Löwdin equation.[82] In general, this equation cannot be reduced to an eigenvalue problem by diagonalizing the matrix λ, although by slight manipulation we can introduce a Hermitian operator with a spectrum of eigenvalues ν corresponding to the vertical IPs.[83] Such construction is afforded by the EKT,[2–5] which provides the connection between the 1- and 2-RDMs of a Coulombic system and its IPs.

The equation for the EKT may be derived by expressing the wavefunction of the $(N - 1)$-electron system as the following linear combination:

$$|\Psi^{N-1}\rangle = \sum_i C_i\hat{a}_i|\Psi^N\rangle. \qquad (6)$$

In Eq. (6), $\hat{a}_i$ is the annihilation operator for an electron in the spin-orbital $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle$ ($\sigma = \alpha, \beta$), $|\Psi^N\rangle$ is the wavefunction of the N-electron system, $|\Psi^{N-1}\rangle$ is the wavefunction of the $(N-1)$-electron system, and $\{C_i\}$ is the set of coefficients to be determined. Optimizing the energy of the state Ψ^{N-1} with respect to the parameters $\{C_i\}$ and subtracting the energy of Ψ^N give the EKT equations as a generalized eigenvalue problem,

$$\mathbf{FC} = \mathbf{\Gamma C}\nu, \tag{7}$$

where ν are the EKT IPs and the metric matrix $\mathbf{\Gamma}$ is the 1-RDM with the occupation numbers along the diagonal and zeros in off-diagonal elements. The transition matrix elements are given by

$$F_{ji} = \langle \Psi^N | \hat{a}_j^\dagger [\hat{\mathcal{H}}, \hat{a}_i] | \Psi^N \rangle. \tag{8}$$

By using a spin-restricted theory, it is not difficult to demonstrate that transition matrix elements $F_{qp} = -\lambda_{qp} = -V_{qp}n_p$. Equation (7) can be transformed by a canonical orthonormalization using $\mathbf{\Gamma}^{-1/2}$. Hence, the diagonalization of the matrix ν whose elements are

$$\nu_{qp} = -\frac{\lambda_{qp}}{\sqrt{n_q n_p}} \tag{9}$$

yields IPs as eigenvalues.

III. RESULTS

In this section, the vertical IPs of a selected set of 30 molecules along with the EAs of a selected group of 10 radical species are presented. All calculations have been carried out using the PNOFID code[85] at the experimental geometries.[84] The accumulated experience indicates that NOF optimum geometries are very close to the experimental ones.[74]

Table I lists the obtained lowest vertical IPs (LVIPs) by PNOF5–EKT together with KT and experimental values. The LVIPs were calculated using the correlation consistent cc-pVDZ contracted GAUSSIAN basis set.[91,92] The differences between both the theoretically obtained values and their corresponding experimental marks are given in parentheses.

It has long been recognized that, in general, there is an excellent agreement between the KT LVIPs and the experimental data because of the fortuitous cancellation of the electron correlation and orbital relaxation effects. A survey of Table I reveals that KT consistently overestimates the LVIPs. Exceptions are Li_2, P_2, HCN, C_2H_2, C_2H_4, C_6H_6, CH_3CClO, and CH_3CN. The prevailing trend is that PNOF5-EKT values improve those obtained by KT. In few cases, however, KT values are not improved by PNOF5-EKT, namely, CH_4, HCN, CH_3CN, and SiO. Nevertheless, PNOF5-EKT LVIPs move generally closer to experimental data.

A remarkable case is the planar trimethylenemethane (TMM). HF cannot describe correctly diradicals, hence the obtained KT LVIP is hopeless for this molecule. PNOF5 correctly describes diradicals.[57,93] It provides a twofold degenerate strongly occupied orbitals with occupation numbers equal to one, and additionally, the calculated LVIP lies closer to the expected value.

TABLE I. Comparison of the lowest vertical ionization potentials (eV) using the correlation consistent cc-pVDZ basis set. The relative errors with respect to the experimental values are given in parentheses. Mean absolute errors (MAE) are in eV.

Molecule	MO	KT	EKT	EXP[a]
LiH	σ	8.17 (0.27)	7.53 (−0.37)	7.90[b]
Li_2	σ	4.91 (−0.23)	5.20 (0.06)	5.14[c]
N_2	σ_g	17.05 (1.45)	16.45 (0.85)	15.60[d]
F_2	π_g	18.03 (2.16)	17.23 (1.36)	15.87
P_2	π_u	10.03 (−0.59)	10.57 (−0.05)	10.62
HF	π	17.12 (1.00)	16.76 (0.64)	16.12
HCl	π	12.82 (0.05)	12.63 (−0.14)	12.77
CO	σ	14.93 (0.92)	14.16 (0.15)	14.01
SiO	σ	11.78 (0.11)	11.82 (0.15)	11.67
HCN	π	13.37 (−0.24)	13.96 (0.35)	13.61
H_2O	b_1	13.42 (0.80)	13.06 (0.44)	12.62
CO_2	π_g	14.59 (0.81)	13.96 (0.18)	13.78
SO_2	a_1	13.24 (0.74)	13.00 (0.50)	12.50
NH_3	a_1	11.41 (0.59)	11.05 (0.23)	10.82
ClF_3	b_1	14.52 (1.47)	13.53 (0.48)	13.05
CH_4	t_2	14.78 (0.38)	15.14 (0.74)	14.40[d]
C_2H_2	π_u	11.06 (−0.43)	11.61 (0.12)	11.49
C_2H_4	$1b_{3u}$	10.14 (−0.54)	10.87 (0.19)	10.68
H_2CO	b_2	11.84 (0.94)	11.74 (0.84)	10.90
C_6H_6	e_{1g}	9.05 (−0.20)	9.20 (−0.05)	9.25[e]
BrF_5	a_1	14.46 (1.29)	13.62 (0.45)	13.17
CH_3CClO	a'	10.73 (−0.30)	11.13 (0.10)	11.03
CH_3CN	a'	12.43 (−0.03)	12.97 (0.51)	12.46
HCOOH	a'	12.43 (0.93)	12.29 (0.79)	11.50
CH_3OCH_3	b_1	11.36 (1.26)	11.24 (1.14)	10.10
HOC-CHO	a_g	11.75 (1.15)	11.58 (0.98)	10.60
$HCONH_2$	a''	11.20 (1.05)	10.34 (0.19)	10.15
CH_3SH	a	9.56 (0.12)	9.33 (−0.11)	9.44
Li_3O^-	a_1'	0.32 (−0.33)	0.45 (−0.20)	0.65[f]
TMM[g]	a''	5.22 (−1.93)	8.20 (1.05)	7.15[h]
MAE		0.74	0.45	

[a]Experimental value from Ref. 86.
[b]Aadiabatic ionization potential from Ref. 86.
[c]Experimental value from Ref. 87.
[d]Experimental value from Ref. 88.
[e]Experimental value from Ref. 88.
[f]Experimental value from Ref. 89.
[g]TMM stands for trimethylenemethane.
[h]Estimated theoretical value from Ref. 90.

The superior performance of the PNOF5-EKT vs KT is established by carrying out a statistical analysis of the IP MAEs with respect to the experimental values. The MAE for KT is calculated to be 0.74 eV, whereas 0.45 eV has been obtained for PNOF5-EKT.

The use of finite basis sets leads to inaccuracies due to their incompleteness, which undermines ultimately the quality of the calculations. The assessment of the performance of the basis functions for a molecular calculation is therefore an important issue that should be examined with care. We have evaluated the LVIPs of the studied diatomic molecules (LiH, Li_2, F_2, HCl, P_2, SiO, HF, N_2, CO) with PNOF5-EKT and the correlation-consistent basis set series cc-pVXZ (X = D, T, Q, 5).[91,92] Our results are shown in Table II. For comparison, Table II includes also the available experimental data. Inspection of the data collected in this table reveals that for the

TABLE II. Lowest vertical ionization potentials by PNOF5–EKT using the correlation-consistent basis set series cc-pVXZ (X = D, T, Q, 5) and experimental data, in eV.

Molecule	MO	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	EXP[a]
LiH	σ	7.53	7.51	7.53	7.53	7.90[b]
Li_2	σ	5.20	5.23	5.24	5.27	5.14[c]
N_2	σ_g	16.45	16.69	16.71	16.64	15.60[d]
F_2	π_g	17.23	17.51	17.57	17.54	15.87
P_2	π_u	10.57	10.53	10.57	10.57	10.62
HF	π	16.76	17.25	17.37	17.43	16.12
HCl	π	12.63	12.80	12.87	12.87	12.77
CO	σ	14.16	14.19	14.21	14.22	14.01
SiO	σ	11.82	11.88	12.11	12.01	11.67

[a]Experimental data from Ref. 86.
[b]Adiabatic ionization potential from Ref. 86.
[c]Experimental value from Ref. 87.
[d]Experimental value from Ref. 88.

TABLE IV. Comparison of electron affinities (eV) calculated using the augmented correlation-consistent aug-cc-pVTZ basis set and their relative errors, in parentheses, with respect to the experimental values.

Molecule	KT	EKT	EXP[a]
H·	1.24 (0.49)	0.37 (−0.38)	0.75
Li·	−0.80 (−1.42)	0.34 (−0.28)	0.62
F·	4.93 (1.53)	4.64 (1.24)	3.40
Cl·	4.09 (0.48)	3.95 (0.34)	3.61
OH·	2.97 (1.14)	2.69 (0.86)	1.83
CN·	5.24 (1.38)	4.60 (0.74)	3.86
NH_2·	1.33 (0.56)	1.02 (0.25)	0.77
PH_2·	1.23 (−0.03)	1.02 (−0.24)	1.26
SH·	2.58 (0.27)	2.42 (0.11)	2.31
OOH·	1.96 (0.88)	1.62 (0.54)	1.08
MAE	0.82	0.50	

[a]Experimental value from Ref. 86.

selected set of molecules, the LVIPs obtained with the PNOF5-EKT does not yield a better agreement with their corresponding experimental marks, as the size of the basis set improves. Notice that, in general, the values of the LVIPs increase with increasing cardinal number X of the Dunning's basis set, but no reliable extrapolation scheme can be envisaged. On the contrary, for molecules LiH and P_2, the LVIPs obtained with the basis sets cc-pVDZ and cc-pV5Z coincide, and in other cases, like N_2, F_2, and SiO, the LVIPs increase with increasing cardinal number X, and then decrease. In view of these data, it is concluded that the EKT values obtained from the PNOF5 calculations do not show a lot dependence on the basis functions set used, and hence, any decent basis function set can safely be used for the calculations of the LVIPs. Furthermore, it is additionally noticed that the correlation-consistent basis function set series of Dunning does not display a smooth convergence towards the experimental marks.

In Table III, higher vertical IPs (HVIPs) are reported for the N_2 and F_2 molecules using the correlation-consistent basis sets cc-pVDZ and cc-pVTZ. These cases have been chosen due to the fact that KT fails dramatically in describing these ionizations. For the remaining studied systems, the trends observed in HVIPs are similar to those observed for the LVIPs, however, the PNOF5–EKT and KT HVIPs deviate usually more than the LVIPs from the experimental IPs.

It is well known that KT IPs for π_u orbital of N_2 and for the σ_g orbital of F_2 are in reasonable agreement with the experimental data, but the σ_g and π_u IPs are in the wrong order for both molecules (see Table III). PNOF5–EKT calculations, on the contrary, give valence shell IPs in the correct order, and in general a numerical improvement is obtained over KT IPs.

Finally, Table IV collects the calculated EAs for a set of 10 radical atoms and molecules. The EA has been estimated as the negative of the IP of the anionic species, calculated at the geometries of the neutral species. These magnitudes were computed using the aug-cc-pVTZ basis set[91, 92] due to the importance of diffuse functions for describing anionic species. Observe that the calculated EKT EAs are in good agreement with the experimental values, and improve noticeably those obtained by means of the KT. The MAE is calculated to be 0.82 eV for KT, whereas 0.50 eV has been obtained for PNOF5-EKT, similar to the errors obtained for the LVIPs.

The assessment of the performance of basis functions for the EA calculation by PNOF5-EKT has been carried out by inspecting the augmented correlation-consistent basis set series aug-cc-pVXZ (X = D, T, Q, 5) (Refs. 91, 92) for H·, Li·, F·, Cl·, OH·, and SH· radicals. Our results are shown in Table V. For comparison, Table V includes also the available experimental data. Inspection of the data collected in this table reveals that the behavior of EAs is similar to that obtained

TABLE III. Comparison of ionization potentials (eV) and their relative errors, in parentheses, with respect to the experimental values.

Molecule	MO	cc-pVDZ		cc-pVTZ		EXP
		KT	EKT	KT	EKT	
N_2	σ_g	17.05 (1.45)	16.45 (0.85)	17.23 (1.63)	16.69 (1.09)	15.60[a]
	π_u	16.56 (−0.12)	17.34 (0.66)	16.68 (0.00)	17.50 (0.82)	16.68[a]
	σ_u	21.08 (2.30)	20.19 (1.41)	21.18 (2.40)	20.45 (1.67)	18.78[a]
F_2	π_g	18.03 (2.16)	17.23 (1.36)	18.09 (2.22)	17.52 (1.65)	15.87[b]
	π_u	21.95 (3.15)	21.38 (2.58)	22.02 (3.22)	21.64 (2.84)	18.80[b]
	σ_g	20.26 (−0.84)	22.33 (1.23)	20.41 (−0.69)	22.48 (1.38)	21.10[b]

[a]Experimental value from Ref. 8.
[b]Experimental value from Ref. 86.

TABLE V. Electron affinities by PNOF5–EKT using the augmented correlation-consistent basis set series aug-cc-pVXZ (X = D, T, Q, 5) and experiment, in eV.

Molecule	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	EXP[a]
H·	0.34	0.37	0.37	0.38	0.75
Li·	0.18	0.34	0.53	0.55	0.62
F·	4.62	4.64	4.64	4.65	3.40
Cl·	3.94	3.95	3.94	3.92	3.61
OH·	2.64	2.69	2.70	2.70	1.83
SH·	2.41	2.42	2.43	2.41	2.31

[a]Experimental value from Ref. 86.

previously for the LVIPs, i.e., the PNOF5-EKT does not necessarily yield a better agreement with their corresponding experimental data as the size of the basis set improves. In general, the values of the EAs increase with increasing cardinal number X of the Dunning's basis set, but no reliable extrapolation scheme can be envisaged. Notice that for SH·, the EAs obtained with the basis sets aug-cc-pVDZ and aug-cc-pV5Z coincide, and in other cases, like Cl·, the EA increases with increasing cardinal number X, and then decreases. This behavior comes along with that found for the LVIPs and confirms that EKT values are marginally affected by the basis function set employed.

IV. CONCLUSIONS

The recent proposed PNOF5 (Ref. 57) was used to determine vertical IPs for a set of 30 selected molecules at their experimental geometries. Moreover, EAs for a set of 10 selected radicals were estimated as the negative of the corresponding IPs of the anionic species, calculated at the geometries of the neutral species. The IPs and EAs obtained via EKT from PNOF5 method were compared with the experimental values. The agreement between our PNOF5-EKT IPs and EAs and those obtained experimentally is satisfactory, however for higher IPs this agreement is smaller than for the lowest IPs. The PNOF5–EKT method under study provides an improvement in the IPs and EAs over the KT approach. In general, we observed that the overall trends with the introduction of the electronic correlation by PNOF5 are adequate. The reliability of the PNOF5 in the prediction of the studied property has been illustrated and found that it is mildly dependent on the basis function set used. It is confirmed that EKT calculations produce IPs of comparable accuracy but at a substantially lower computational cost than energy-difference calculations.

[1]T. A. Koopmans, Physica (Amsterdam) **1**, 104 (1933).
[2]O. W. Day, D. W. Smith, and C. Garrod, Int. J. Quantum Chem. Symp. **8**, 501 (1974).
[3]O. W. Day, D. W. Smith, and R. C. Morrison, J. Chem. Phys. **62**, 115 (1975).
[4]D. W. Smith and O. W. Day, J. Chem. Phys. **62**, 113 (1975).
[5]M. M. Morrell, R. G. Parr, and M. Levy, J. Chem. Phys. **62**, 549 (1975).
[6]J. Katriel and E. R. Davidson, Proc. Natl. Acad. Sci. U.S.A. **77**, 4403 (1980).
[7]R. C. Morrison, J. Chem. Phys. **96**, 3718 (1992).
[8]R. C. Morrison and G. Liu, J. Comp. Chem. **13**, 1004 (1992).
[9]R. C. Morrison, J. Chem. Phys. **99**, 6221 (1993).
[10]D. Sundholm and J. Olsen, J. Chem. Phys. **98**, 3999 (1993).
[11]J. Olsen and D. Sundholm, Chem. Phys. Lett. **288**, 282 (1998).
[12]K. Pernal and J. Cioslowski, J. Chem. Phys. **114**, 4359 (2001).
[13]J. Cioslowski, P. Piskorz, and G. Liu, J. Chem. Phys. **107**, 6804 (1997).
[14]T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).
[15]M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[16]S. M. Valone, J. Chem. Phys. **73**, 1344 (1980).
[17]M. Levy, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. J. Smith (Reidel, Dordrecht, 1987), pp. 479–498.
[18]J. Cioslowski, J. Chem. Phys. **123**, 164106 (2005).
[19]H. Appel and E. K. U. Gross, EPL **92**, 23001 (2010).
[20]E. Cancès and K. Pernal, J. Chem. Phys. **128**, 134108 (2008).
[21]F. Feixas, E. Matito, M. Duran, M. Sola, and B. Silvi, J. Chem. Theory Comput. **6**, 2736 (2010).
[22]F. Feixas, E. Matito, M. Duran, M. Sola, and B. Silvi, J. Chem. Theory Comput. **7**, 1231 (2011) (Erratum).
[23]K. Giesbertz, E. Baerends, and O. V. Gritsenko, Phys. Rev. Lett. **101**, 033004 (2008).
[24]K. J. H. Giesbertz, K. Pernal, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **130**, 114104 (2009).
[25]K. J. H. Giesbertz and E. J. Baerends, J. Chem. Phys. **132**, 194108 (2010).
[26]K. Giesbertz, O. V. Gritsenko, and E. Baerends, Phys. Rev. Lett. **105**, 013002 (2010).
[27]N. Helbig, N. N. Lathiotakis, M. Albrecht, and E. K. U. Gross, Europhys. Lett. **77**, 67003 (2007).
[28]N. Helbig, N. N. Lathiotakis, and E. Gross, Phys. Rev. A **79**, 022504 (2009).
[29]N. Helbig, I. V. Tokatly, and A. Rubio, Phys. Rev. A **81**, 022504 (2010).
[30]N. Helbig, G. Theodorakopoulos, and N. N. Lathiotakis, J. Chem. Phys. **135**, 054109 (2011).
[31]N. Helbig, J. Fuks, I. Tokatly, H. Appel, E. Gross, and A. Rubio, Chem. Phys. **391**, 1 (2011).
[32]N. N. Lathiotakis, N. Helbig, and E. K. U. Gross, Phys. Rev. B **75**, 195120 (2007).
[33]N. N. Lathiotakis and M. A. L. Marques, J. Chem. Phys. **128**, 184103 (2008).
[34]N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. G. Eich, M. A. L. Marques, and E. K. U. Gross, Phys. Rev. A **79**, 040501(R) (2009).
[35]N. N. Lathiotakis, N. Helbig, A. Zacarias, and E. K. U. Gross, J. Chem. Phys. **130**, 064109 (2009).
[36]N. N. Lathiotakis, S. Sharma, N. Helbig, J. K. Dewhurst, M. A. L. Marques, F. Eich, T. Baldsiefen, A. Zacarias, and E. K. U. Gross, Z. Phys. Chem. **224**, 467 (2010).
[37]N. N. Lathiotakis, N. I. Gidopoulos, and N. Helbig, J. Chem. Phys. **132**, 084105 (2010).
[38]P. Leiva and M. Piris, Int. J. Quantum Chem. **107**, 1 (2007).
[39]X. Lopez, M. Piris, J. M. Matxain, and J. M. Ugalde, Phys. Chem. Chem. Phys. **12**, 12931 (2010).
[40]X. Lopez, F. Ruipérez, M. Piris, J. M. Matxain, and J. M. Ugalde, ChemPhysChem **12**, 1061 (2011).
[41]X. Lopez, M. Piris, J. M. Matxain, F. Ruipérez, and J. M. Ugalde, ChemPhysChem **12**, 1673 (2011), see http://www.ncbi.nlm.nih.gov/pubmed/21626644.
[42]M. A. L. Marques and N. N. Lathiotakis, Phys. Rev. A **77**, 032509 (2008).
[43]J. M. Matxain, M. Piris, X. Lopez, and J. Ugalde, Chem. Phys. Lett. **499**, 164 (2010).
[44]J. M. Matxain, M. Piris, F. Ruipérez, X. Lopez, and J. M. Ugalde, Phys. Chem. Chem. Phys. **13**, 20129 (2011).
[45]K. Pernal, K. Giesbertz, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **127**, 214101 (2007).
[46]K. Pernal, O. V. Gritsenko, and E. J. Baerends, Phys. Rev. A **75**, 012506 (2007).

[47] K. Pernal and J. Cioslowski, Phys. Chem. Chem. Phys. **9**, 5956 (2007).

[48] K. Pernal, Phys. Rev. A **81**, 052511 (2010).

[49] M. Piris, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **126**, 214103 (2007).

[50] M. Piris, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **128**, 134102 (2008).

[51] M. Piris, X. Lopez, and J. M. Ugalde, Int. J. Quantum Chem. **108**, 1660 (2008).

[52] M. Piris, J. M. Matxain, and J. M. Ugalde, J. Chem. Phys. **129**, 014108 (2008).

[53] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **131**, 021102 (2009).

[54] M. Piris and J. M. Ugalde, J. Comput. Chem. **30**, 2078 (2009).

[55] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **132**, 031103 (2010).

[56] M. Piris, J. M. Matxain, X. Lopez, and J. M. Ugalde, J. Chem. Phys. **133**, 111101 (2010).

[57] M. Piris, X. Lopez, F. Ruipérez, J. M. Matxain, and J. M. Ugalde, J. Chem. Phys. **134**, 164102 (2011).

[58] A. Putaja and E. Räsänen, Phys. Rev. B **84**, 035104 (2011).

[59] R. Requist and O. Pankratov, Phys. Rev. B **77**, 235121 (2008).

[60] R. Requist and O. Pankratov, Phys. Rev. A **81**, 042519 (2010).

[61] D. R. Rohr, K. Pernal, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **129**, 164105 (2008).

[62] D. R. Rohr, J. Toulouse, and K. Pernal, Phys. Rev. A **82**, 052502 (2010).

[63] D. R. Rohr and K. Pernal, J. Chem. Phys. **135**, 074104 (2011).

[64] S. Sharma, J. K. Dewhurst, N. N. Lathiotakis, and E. K. U. Gross, Phys. Rev. B **78**, 201103(R) (2008).

[65] E. Tölö and A. Harju, Phys. Rev. B **81**, 075321 (2010).

[66] M. Piris, in *Reduced-Density-Matrix Mechanics: With Applications to Many-Electron Atoms and Molecules*, edited by D. A. Mazziotti (Wiley, Hoboken, NJ, 2007), Chap. 14, pp. 387–427.

[67] M. Piris and P. Otto, Int. J. Quantum Chem. **94**, 317 (2003).

[68] M. Piris and P. Otto, Int. J. Quantum Chem. **102**, 90 (2005).

[69] D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998).

[70] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **110**, 2800 (1999).

[71] D. A. Mazziotti, Phys. Rev. Lett. **101**, 253002 (2008).

[72] A. Sand, C. A. Schwerdtfeger, and D. A. Mazziotti, J. Chem. Phys. **136**, 034112 (2012).

[73] M. Piris, Int. J. Quantum Chem. **106**, 1093 (2006).

[74] M. Piris, "A natural orbital functional based on an explicit approach of the two-electron cumulant," Int. J. Quantum Chem. (in press).

[75] J. M. Matxain, M. Piris, J. M. Mercero, X. Lopez, and J. Ugalde, Chem. Phys. Lett. **531**, 272 (2012).

[76] K. Pernal and J. Cioslowski, Chem. Phys. Lett. **412**, 71 (2005).

[77] P. Leiva and M. Piris, J. Mol. Struc.: THEOCHEM **770**, 45 (2006).

[78] M. A. Buijse and E. J. Baerends, Mol. Phys. **100**, 401 (2002).

[79] O. V. Gritsenko, K. Pernal, and E. J. Baerends, J. Chem. Phys. **122**, 204102 (2005).

[80] D. Farnum, D. A. Mazziotti, Chem. Phys. Lett. **400**, 90 (2004).

[81] D. A. Mazziotti, Chem. Rev. **112**, 244 (2012).

[82] P. O. Lowdin, Phys. Rev. **97**, 1474 (1955).

[83] R. A. Donnelly, J. Chem. Phys. **71**, 2874 (1979).

[84] *NIST Computational Chemistry Comparison and Benchmark Database.* NIST Standard Reference Database Vol. 101, Release 15b, edited by R. D. Johnson, III (NIST, 2011), see http://cccbdb.nist.gov/.

[85] M. Piris, PNOFID, see http://www.ehu.es/mario.piris/Software.

[86] S. Lias, H. Rosenstock, K. Draxl, B. Steiner, J. Herron, J. Holmes, R. Levin, J. Liebman, and S. Kafafi, *Ionization Energetics data, NIST Chemistry WebBook*, NIST Standard Reference Database Vol. 69 (NIST, 2011), see http://webbook.nist.gov/chemistry.

[87] D. R. Yarkony, J. Chem. Phys. **90**, 7164 (1989).

[88] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules* (Halsted, 1981).

[89] M. Gutowski and J. Simons, J. Phys. Chem. **98**, 8326 (1994).

[90] J. H. Davis and W. A. Goddard III, J. Am. Chem. Soc. **98**, 303 (1976).

[91] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[92] D. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).

[93] X. Lopez, M. Piris, J. M. Matxain, F. Ruipérez, and J. M. Ugalde, "Performance of PNOF5 for radical formation reactions: Hydrogen abstraction, C-C and O-O homolytic bond cleavage in selected molecules," J. Chem. Theory Comput. (in press).