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published in
Journal of Chemical Physics
2002

DOI (link to publisher)
10.1063/1.1430255

document version
Publisher's PDF, also known as Version of record

Link to publication in VU Research Portal

citation for published version (APA)
Chong, D. P., Gritsenko, O. V., & Baerends, E. J. (2002). Interpretation of the Kohn-Sham orbital energies as approximate vertical ionization potentials. *Journal of Chemical Physics*, *116*(5), 1760-1772. https://doi.org/10.1063/1.1430255

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JOURNAL OF CHEMICAL PHYSICS VOLUME 116, NUMBER 5 1 FEBRUARY 2002

ARTICLES

Interpretation of the Kohn–Sham orbital energies as approximate vertical ionization potentials

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(Received 9 July 2001; accepted 5 November 2001)

Theoretical analysis and results of calculations are put forward to interpret the energies $-\epsilon_k$ of the occupied Kohn–Sham (KS) orbitals as approximate but rather accurate *relaxed* vertical ionization potentials (VIPs) I_k. Exact relations between ϵ_k and I_k are established with a set of linear equations for the ϵ_k, which are expressed through I_k and the matrix elements $\epsilon_k^{\mathrm{resp}}$ of a component of the KS exchange-correlation (xc) potential v_{xc}, the response potential v_{resp}. Although $-I_k$ will be a leading contribution to ϵ_k, other $I_{j\neq k}$ do enter through coupling terms which are determined by the overlaps between the densities of the KS orbitals as well as by overlaps between the KS and Dyson orbital densities. The orbital energies obtained with "exact" KS potentials are compared with the experimental VIPs of the molecules N_2, CO, HF, and H_2O. Very good agreement between the accurate $-\epsilon_k$ of the outer valence KS orbitals and the corresponding VIPs is established. The average difference, approaching 0.1 eV, is about an order of magnitude smaller than for HF orbital energies. The lower valence KS levels are a few eV higher than the corresponding $-I_k$, and the core levels some 20 eV, in agreement with the theoretically deduced upshift of the KS levels compared to $-I_k$ by the response potential matrix elements. Calculations of 64 molecules are performed with the approximate v_{xc} obtained with the statistical averaging of (model) orbitals potentials (SAOP) and the calculated ϵ_k are compared with 406 experimental VIPs. Reasonable agreement between the SAOP $-\epsilon_k$ and the outer valence VIPs is found with an average deviation of about 0.4 eV. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1430255]

I. INTRODUCTION

A long-standing problem of the one-electron Kohn–Sham (KS) approach[1] of density functional theory (DFT) is the physical interpretation of its key quantities, the KS orbitals ψ_k and the orbital energies ϵ_k. It has been argued many times[2–4] that the KS orbitals are physically meaningful owing to the physical nature of the KS potential, which incorporates such important terms as the Coulomb hole potential and the so-called kinetic (correlation) potential. They have certain advantages over Hartree–Fock orbitals and can be recommended for use in the MO theoretical analyses of quantum chemistry.[5] The situation is less clear for the KS orbital energies. Only the energy ϵ_{HOMO} of the highest occupied molecular orbital (HOMO) ψ_H is known to have a physical meaning as (minus) the lowest vertical ionization potential (VIP)[6–12]

$$\epsilon_H = -I_H, \tag{1.1}$$

while the occupied KS orbitals produce the total electronic density ρ,

$$\rho(\mathbf{r}_1) = \sum_i^H 2|\psi_i(\mathbf{r}_1)|^2, \tag{1.2}$$

where we specialize to closed shell systems with N electrons in $H=N/2$ doubly occupied orbitals. With respect to the other KS orbital energies, a standard view expressed in the literature is that they are merely auxiliary quantities which, in general, have no definite physical meaning. Parr and Yang[13] are adamant on this physical meaning: "There is none." On the other hand, the empirical observation has been made frequently that approximate KS orbital energies [from the local-density (LDA) or one of the generalized gradient (GGA) approximations] exhibit a large (several eV) but fairly uniform shift with respect to the experimental ionization energies.[14,15] However, even with a constant shift applied to the orbital energies significant deviations with IPs (up to an eV) remain. In the one-electron Hartree–Fock (HF) theory a physical meaning for the orbital energies is provided by Koopman's theorem.[16] According to this theorem, the energies ϵ_k^{HF} of the occupied HF orbitals are equal to (minus) the unrelaxed VIPs $\tilde{I}_k$. With the same neglect of relaxation effects in the cationic states, the HF orbitals ψ_k^{HF} represent the Dyson orbitals d_k, the latter being defined from the overlap integral

$$d_k(\mathbf{x}_1) = \sqrt{N} \int \Psi_k^{(N-1)*}(\mathbf{x}_2,\ldots,\mathbf{x}_N) \times \Psi^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\, d\mathbf{x}_2 \ldots d\mathbf{x}_N \tag{1.3}$$

between the wave function Ψ^N of the ground state of a neutral N electron system and the wave function Ψ_k^{N-1} of the cationic excited state. The coordinates $\mathbf{x}_i$ consist of spatial and spin coordinates, $\mathbf{x}=\mathbf{r},s$. For the closed shell molecules we are dealing with, the ion states are spin doublets and the Dyson spin–orbitals will just be up and down spin–orbitals with identical spatial parts. It is interesting to note that neither self-interaction corrected KS orbital energies[17] nor exact exchange Kohn–Sham orbital energies[18] exhibit the shift of several eV mentioned above for the LDA and GGA orbital energies, but are characterized by similar deviations from experimental IPs as HF orbital energies (in the eV order of magnitude).

The situation is however drastically improved when the true Kohn–Sham orbital energies are considered. In this paper theoretical analysis and results of calculations are shown to afford an interpretation of the energies $-\epsilon_k$ of the occupied KS orbitals as approximate but rather accurate *relaxed* VIPs I_k

$$\epsilon_k \approx -I_k . \tag{1.4}$$

The agreement with experimental IPs (at the 0.1 eV level for the upper valence levels) is roughly an order of magnitude better than is the case for HF or exact exchange Kohn–Sham orbital energies. In Sec. II an analysis of the KS exchange-correlation (xc) potential v_{xc} is performed with partitioning into the xc-hole $v_{\mathrm{xc}}^{\mathrm{hole}}$, kinetic correlation $v_{c,\mathrm{kin}}$, and response v_{resp} potentials. From an expansion of v_{resp} in terms of the KS and Dyson orbitals, a set of linear equations for the orbital energies ϵ_k is obtained, which expresses them through the VIPs I_k and the contributions $\epsilon_k^{\mathrm{resp}}=\langle\varphi_k|v_{\mathrm{resp}}|\varphi_k\rangle$ to ϵ_k. Making use of the Krieger–Li–Iafrate (KLI)[19] and related[20] approximations to v_{resp}, it is argued that the leading terms are those with I_k, so that ϵ_k approximately represent VIPs. Section III compares for the molecules N_2, CO, HF, and H_2O the energies ϵ_k, obtained with accurate KS potentials constructed from accurate *ab initio* densities, to the experimental VIPs I_k determined with photoelectron spectroscopy. The accurate $-\epsilon_k$ of the valence orbitals provide a very good estimate of the corresponding I_k, with average deviations of only 0.02–0.18 eV. Section IV presents calculations of 64 molecules with the approximate xc potential obtained with the statistical averaging of (model) orbital potentials (SAOP).[21–23] The calculated orbital energies are compared with 406 experimental VIPs obtained with molecular photoelectron spectroscopy. The approximate $-\epsilon_k$ reproduce the corresponding I_k uniformly well for various types of molecules with an average deviation of ca. 0.4 eV. In Sec. V the implication of the present results for the KS theory, its development and its applications are discussed and the conclusions are drawn.

II. RELATIONS BETWEEN I_k and ϵ_k

The KS orbital energies ϵ_k are defined by the one-electron equations

$$\{-\tfrac{1}{2}\nabla^2+v_{\mathrm{ext}}(\mathbf{r}_1)+v_{\mathrm{Coul}}(\mathbf{r}_1)+v_{\mathrm{xc}}(\mathbf{r}_1)\}\psi_k(\mathbf{r}_1) = \epsilon_k\psi_k(\mathbf{r}_1), \tag{2.1}$$

where v_{ext} is the external potential, v_{Coul} is the Hartree potential of the electrostatic electron repulsion, and v_{xc} is the xc potential. We take the simple case of closed shell molecules with equal potentials for spin–up and spin–down electrons, so no spin labels are attached. In its turn, v_{xc} can be partitioned as follows:[3,24,25]

$$v_{\mathrm{xc}}(\mathbf{r}_1)=v_{\mathrm{xc}}^{\mathrm{hole}}(\mathbf{r}_1)+v_{c,\mathrm{kin}}(\mathbf{r}_1)+v_{\mathrm{resp}}(\mathbf{r}_1). \tag{2.2}$$

In (2.2) $v_{\mathrm{xc}}^{\mathrm{hole}}$ is the xc-hole potential defined with the pair-correlation function $g(\mathbf{r}_1,\mathbf{r}_2)$

$$v_{\mathrm{xc}}^{\mathrm{hole}}(\mathbf{r}_1)=\int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)[g(\mathbf{r}_1,\mathbf{r}_2)-1]}{|\mathbf{r}_1-\mathbf{r}_2|}, \tag{2.3}$$

$v_{c,\mathrm{kin}}$ is the kinetic correlation potential, which can be expressed either in terms of first or second derivatives of the exact γ and KS γ_s first-order density matrices[3,24] where the spatial one-electron density matrix is defined as $\gamma(\mathbf{r}_1,\mathbf{r}_1')=\int ds_1\ \gamma(\mathbf{r}_1 s_1,\mathbf{r}_1' s_1)=\gamma^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_1')+\gamma^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_1')$ and $\rho(\mathbf{r}_1)=\rho^{\alpha}(\mathbf{r}_1)+\rho^{\beta}(\mathbf{r}_1)$,

$$\begin{aligned} v_{c,\mathrm{kin}}(\mathbf{r}_1)&=\frac{1}{2\rho(\mathbf{r}_1)}[-\nabla_1^2\gamma(\mathbf{r}_1',\mathbf{r}_1)|_{\mathbf{r}_1'=\mathbf{r}_1} \\ &\quad+\nabla_1^2\gamma_s(\mathbf{r}_1',\mathbf{r}_1)|_{\mathbf{r}_1'=\mathbf{r}_1}] \\ &=\frac{1}{2\rho(\mathbf{r}_1)}[\nabla_1'\cdot\nabla_1\gamma(\mathbf{r}_1',\mathbf{r}_1)|_{\mathbf{r}_1'=\mathbf{r}_1} \\ &\quad-\nabla_1'\cdot\nabla_1\gamma_s(\mathbf{r}_1',\mathbf{r}_1)|_{\mathbf{r}_1'=\mathbf{r}_1}], \end{aligned} \tag{2.4}$$

and v_{resp} is the response potential defined with the functional derivatives of $g(\mathbf{r}_1,\mathbf{r}_2)$ and $v_{c,\mathrm{kin}}(\mathbf{r}_1)$,

$$\begin{aligned} v_{\mathrm{resp}}(\mathbf{r}_1)&=\int d\mathbf{r}_2\ d\mathbf{r}_3 \frac{\rho(\mathbf{r}_2)\rho(\mathbf{r}_3)}{|\mathbf{r}_2-\mathbf{r}_3|}\frac{\delta g(\mathbf{r}_2,\mathbf{r}_3)}{\delta\rho(\mathbf{r}_1)} \\ &\quad+\int d\mathbf{r}_2\ \rho(\mathbf{r}_2)\frac{\delta v_{c,\mathrm{kin}}(\mathbf{r}_2)}{\delta\rho(\mathbf{r}_1)}. \end{aligned} \tag{2.5}$$

It is v_{resp}, which contains in its structure relations between the ionization potentials I_k and orbital energies ϵ_k. In order to obtain these relations, we use an alternative to the expression (2.5) for v_{resp},[24,25]

$$v_{\mathrm{resp}}(\mathbf{r}_1)=v^{N-1}(\mathbf{r}_1)-v_s^{N-1}(\mathbf{r}_1) \tag{2.6}$$

in terms of the potentials v^{N-1} and v_s^{N-1}, which describe the $N-1$ electron system in the presence of the reference electron at $\mathbf{r}_1$. In particular, v^{N-1} is defined with the "interacting" conditional probability amplitude Φ (Ref. 26) the square of which is the probability to find electrons $2-N$ at "positions" $\mathbf{x}_2-\mathbf{x}_N$,

$$\Phi(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)=\frac{\Psi^N(\mathbf{x}_1,\ldots,\mathbf{x}_N)}{\sqrt{\rho(\mathbf{x}_1)/N}}, \tag{2.7}$$

as follows:

$$v^{N-1}(\mathbf{r}_1)=E^{N-1}(\mathbf{r}_1)-E_0^{N-1}, \tag{2.8}$$

where $E^{N-1}(\mathbf{r}_1)$ is the energy expectation value of the system of $N-1$ electrons, if the additional reference electron is at $\mathbf{r}_1$ (with either α or β spin)

$$E^{N-1}(\mathbf{r}_1)=\int \Phi^*(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)H^{N-1}\Phi \times(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)d\mathbf{x}_2\ldots d\mathbf{x}_N. \tag{2.9}$$

[$E^{N-1}(\mathbf{x}_1)$ will be the same for an up–spin and a down–spin electron, hence the spin label is omitted.] In (2.7) Ψ^N is the ground-state wave function of the N electron interacting system, in (2.8) E_0^{N-1} is the ground-state energy of the $N-1$ electron interacting system, and in (2.9) H^{N-1} is the Hamiltonian of the $N-1$ electron system.

In its turn, the potential v_s^{N-1} is defined in the same way with the "noninteracting" conditional probability amplitude Φ_s,

$$\Phi_s(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)=\frac{\Psi_s^N(\mathbf{x}_1,\ldots,\mathbf{x}_N)}{\sqrt{\rho(\mathbf{x}_1)/N}}, \tag{2.10}$$

$$v_s^{N-1}(\mathbf{r}_1)=E_s^{N-1}(\mathbf{r}_1)-E_{s,0}^{N-1}, \tag{2.11}$$

$$E_s^{N-1}(\mathbf{r}_1)=\int \Phi_s^*(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)H_s^{N-1}\Phi_s \times(\mathbf{x}_2,\ldots,\mathbf{x}_N|\mathbf{x}_1)d\mathbf{x}_2\ldots d\mathbf{x}_N. \tag{2.12}$$

In (2.10)–(2.12) Ψ_s^N is the KS determinant, the ground-state wave function of the N electron noninteracting KS system, H_s^{N-1} is the $N-1$ electron KS Hamiltonian [using the potential $v_s(\mathbf{r})$ of the N-electron KS system] and $E_{s,0}^{N-1}$ is the energy of the $N-1$ electron noninteracting KS system,

$$E_{s,0}^{N-1}=\sum_{i=1}^{H} 2\epsilon_i-\epsilon_H \tag{2.13}$$

calculated with the determinant Ψ_s^{N-1}, which is generated from Ψ_s^N by the annihilation of one electron from the HOMO ψ_H.

It is essential for our further analysis, that the "interacting" conditional energies $E^{N-1}(\mathbf{r}_1)$ can be conveniently expanded[24] in terms of the Dyson orbitals d_i of (1.3),

$$E^{N-1}(\mathbf{r}_1)=\sum_i \frac{2|d_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}E_i^{N-1}. \tag{2.14}$$

The coefficients are just the total energies of cationic states E_i^{N-1}. We will assume that in the summation of (2.14) the H primary ionizations occur first. These primary ionizations are characterized by wave functions that can be reasonably well approximated by an orbital ionization, without further excitations. If there would be a strong configuration mixing in either the ground state or an ionized state, this identification of primary ionizations might not be possible. If it is possible, the Dyson orbitals of the primary ionizations will resemble the occupied Hartree–Fock orbitals (and the Kohn–Sham orbitals). One of the properties of the Dyson orbitals is that their squares sum up to the total density,

$$\sum_i 2|d_i(\mathbf{r}_1)|^2=\rho(\mathbf{r}_1), \tag{2.15}$$

so

$$v^{N-1}(\mathbf{r}_1)=E^{N-1}(\mathbf{r}_1)-E_0^{N-1} =\sum_i \frac{2|d_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}(E_i^{N-1}-E_0^{N-1}).$$

The "noninteracting" conditional energy $E_s^{N-1}(\mathbf{r}_1)$ can be expanded in an analogous manner in terms of the KS orbitals[25,27]

$$E_s^{N-1}(\mathbf{r}_1)=\sum_i \frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}E_{s,i}^{N-1}, \tag{2.16}$$

where the KS orbitals ψ_i coincide with the Dyson orbitals of the noninteracting system

$$\psi_k(\mathbf{x}_1)=\sqrt{N}\int \Psi_{s,k}^{(N-1)*}(\mathbf{x}_2,\ldots,\mathbf{x}_N) \times\Psi_s^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)d\mathbf{x}_2\ldots d\mathbf{x}_N. \tag{2.17}$$

It is to be noted that this overlap is zero if $\Psi_{s,k}^{N-1}$ differs in more than one orbital from Ψ_s^N, i.e., when the ion state is not a primary one, consisting of removal of an electron from one of the occupied KS orbitals, but contains in addition an excitation of another electron into a virtual orbital. In agreement with this, the total density consists of a summation over just the $N/2=H$ occupied KS orbitals,

$$\sum_{i=1}^{H} 2|\psi_i(\mathbf{r}_1)|^2=\rho(\mathbf{r}_1) \tag{2.18}$$

and the summation in (2.16) will also be restricted to H terms, which may be written, using $E_{s,i}^{N-1}=E_{s,0}^{N}-\epsilon_i$,

$$E_s^{N-1}(\mathbf{r}_1)=\sum_{i=1}^{H} \frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1}(E_{s,0}^{N}-\epsilon_i) =E_{s,0}^{N}-\sum_{i=1}^{H} \frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}\epsilon_i \tag{2.19}$$

so

$$v_s^{N-1}(\mathbf{r}_1)=E_s^{N-1}(\mathbf{r}_1)-E_{s,0}^{N-1}=\sum_{i=1}^{H} \frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}(\epsilon_H-\epsilon_i) \tag{2.20}$$

and

$$v^{\mathrm{resp}}(\mathbf{r}_1)=v^{N-1}(\mathbf{r}_1)-v_s^{N-1}(\mathbf{r}_1)$$
$$=\sum_i \frac{2|d_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}I_i+\sum_{i=1}^{H}\frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}\epsilon_i, \qquad (2.21)$$

where we have used (1.1).

Finally, integrating (2.21) with the orbital density $|\psi_k(\mathbf{r}_1)|^2$, we obtain a set of $N/2$ linear equations for the lowest orbital energies ϵ_i,

$$\sum_i^H M_{ki}\epsilon_i=-\sum_i P_{ki}I_i+\epsilon_k^{\mathrm{resp}} \qquad (2.22)$$

or, in matrix form,

$$\mathbf{M}\boldsymbol{\epsilon}=-\mathbf{PI}+\boldsymbol{\epsilon}^{\mathrm{resp}}, \qquad (2.23)$$

where $\mathbf{M}$ is an $H\times H$ matrix with elements

$$M_{ki}=2\int\frac{|\psi_k(\mathbf{r}_1)|^2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}d\mathbf{r}_1, \qquad (2.24)$$

and $\mathbf{P}$ is an $H\times\infty$ matrix with elements

$$P_{ki}=2\int\frac{|\psi_k(\mathbf{r}_1)|^2|d_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}d\mathbf{r}_1, \qquad (2.25)$$

where we let the first H columns of $\mathbf{P}$ correspond to the Dyson orbitals of the primary ionizations. The elements of the vectors $\mathbf{I}$ and $\boldsymbol{\epsilon}^{\mathrm{resp}}$ are the ionization energies I_k and the matrix elements

$$\epsilon_k^{\mathrm{resp}}=\int|\psi_k(\mathbf{r}_1)|^2 v_{\mathrm{resp}}(\mathbf{r}_1)d\mathbf{r}_1 \qquad (2.26)$$

of the response potential, respectively.

A formal solution of (2.23) is obtained as

$$\boldsymbol{\epsilon}=-\mathbf{M}^{-1}\mathbf{PI}+\mathbf{M}^{-1}\boldsymbol{\epsilon}^{\mathrm{resp}}. \qquad (2.27)$$

Note, that (2.27) are exact relations between ϵ_i and I_j, which involve also contributions to ϵ_i from v_{resp}, the latter potential being defined independently as the functional derivative (2.5).

In the next section it will be demonstrated numerically that the KS ϵ_i are close to the I_i, in particular for valence levels. This result may be anticipated from Eq. (2.27) on the following grounds. First, from what is known about v_{resp}[20,25,28] it is possible to infer that the last term makes a small contribution. It has been observed in atoms that v_{resp} has a typical steplike structure, being almost constant within an atomic shell and stepping up to the next "plateau" when crossing the border region to the next inner shell. This has been explained from electron exchange and correlation effects.[28] The step height is very low in the valence region (being essentially zero in the HOMO region) and becomes sizeable in the deeper shells. The step heights in those shells have been found to be approximately $K\sqrt{\epsilon_N-\epsilon_i}$, with K roughly estimated at 1.99 (in eV).[20] This would lead us to expect that the contributions of the last term might be negligible for the upper valence levels, but would be significant, though much smaller than the actual $-\epsilon_i$, for the deeper levels. This may be substantiated by considering the method of Krieger, Li, and Iafrate,[19] who obtained as an approximation to the KS potential in the exchange-only case the exchange potential v_x^{KLI} with the response part

$$v_{\mathrm{resp}}^{\mathrm{KLI}}(\mathbf{r}_1)=\sum_i^{N/2}\frac{2|\psi_i(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}w_i. \qquad (2.28)$$

This shows the step structure; in regions where the orbital ψ_i dominates, $2|\psi_i(\mathbf{r}_1)|^2\approx\rho(\mathbf{r}_1)$ and the potential is approximately equal to the constant w_i. The constant for the HOMO, w_H, is zero in the KLI method by construction. It is clear that we can write the $\boldsymbol{\epsilon}^{\mathrm{resp}}$ vector in the KLI approximation as $\boldsymbol{\epsilon}^{\mathrm{resp}}=\mathbf{Mw}$, so

$$\boldsymbol{\epsilon}\approx-\mathbf{M}^{-1}\mathbf{PI}+\mathbf{w}. \qquad (2.29)$$

The KLI constants are usually quite small for the upper valence levels, but they are in the 4–5 eV range for *2s* based levels (IPs ca. 35 eV) and are roughly 30, 35, 40 eV for the *1s* levels of C, N, O, F, respectively (IPs approximately 300, 410, 540, and 695 eV). This is an indication for the accuracy with which we may expect the ϵ_i to approximate the I_i for the deeper levels. We may actually expect the agreement to be a bit better rather than being worse, for the following reasons. If the KS orbitals would be identical to the Dyson orbitals of the primary ionizations, the first H columns of the $\mathbf{P}$ matrix would be just the $\mathbf{M}$ matrix. $\mathbf{M}^{-1}\mathbf{P}$ would consist of a leading $H\times H$ unit matrix plus small elements in the remaining columns when the overlap of the KS orbital charge distributions $|\psi_i|^2$ with the higher Dyson orbital charge distributions $|d_k|^2$ would be small (the higher Dyson orbital charge distributions themselves may be very small, see below). It has been speculated[29] that indeed the KS orbitals might be good approximations to the Dyson orbitals corresponding to the primary ionizations. Very recently, it was found[30] for a particular case (the planar D_{3h} Cu_3Cl_3 molecule), where HF and Dyson orbitals are significantly different, than an approximate (B3LYP) KS orbital was indeed closer to the Dyson orbital than the HF orbital was. In case the KS orbitals are good approximations to Dyson orbitals we may write approximately

$$\epsilon_i\approx-I_i+w_i-\sum_{j=H+1}^{\infty}(\mathbf{M}^{-1}\mathbf{P})_{ij}I_j. \qquad (2.30)$$

The positive second term and negative third term will partly cancel each other. As an example we may consider two-electron closed shell systems like He and H_2, which will have a 1×1 $\mathbf{M}$ matrix, and M_{11} reduces to the normalization integral of ψ_1, i.e., $M_{11}=1$. The values of the 1,1 matrix elements of the response potential are known from Ref. 24, being 1.61 eV and 0.98 eV for He and H_2, respectively, while $\epsilon_1 = -I_1$. The matrix elements P_{1i} become the normalization integrals of the Dyson orbitals, the so-called spectroscopic constants, which are all smaller than 1 since they are all positive and their sum should be 1 (half the number of electrons). For ionizations in the outer valence region the normalization integral of the first Dyson orbital is expected to be rather close to 1, and those for the higher Dyson orbitals are much smaller, being related to the intensities of the satellites to the primary ionization in the photoelectron spectrum. According to the exact expression

$$\epsilon_1 = -I_1 = -P_{11} I_1 + v_1^{\mathrm{resp}} - \sum_{i=2}^{\infty} P_{1i} I_i \tag{2.31}$$

exact cancellation of the second and third term to the right-hand side is not possible, since in that case we would have $P_{11}=1$, meaning all $P_{1i}(i>1)=0$, which is inconsistent with the third term contributing $-v_1^{\mathrm{resp}}$. In this example the value $P_{11}<1$ will necessarily make the first term not negative enough, which is aggravated by the positive v_1^{resp}, which is then corrected by the compensating effect of the third term. In this case it actually has to overcompensate v_1^{resp} so that ϵ_1 becomes the exact VIP in spite of the first term being not negative enough. This example shows how some "error compensation" may make the total error smaller than the error due to any of the three individual terms. Note that the error compensation we are considering concerns a term like v_1^{resp} which is already small (1.61 eV) compared to the total I_1 of 24.59 eV. In the case of H_2 $v_1^{\mathrm{resp}}=0.98$ is small compared to $I_1=15.94$ eV. More definitive estimates of the contributions of the individual terms and the extent of error cancellation will have to come from explicit calculations of the **M** and **P** matrices using accurate KS orbitals and Dyson orbitals.

The above arguments are only qualitative. In the next section these qualitative inferences will be tested with actual KS orbital energy calculations.

III. ϵ_i OF ACCURATE KS POTENTIALS VERSUS EXPERIMENTAL VIPS

Rather accurate KS orbital energies ϵ_k can be obtained with KS potentials constructed from highly accurate *ab initio* (CI) densities, the corresponding calculations for molecules have been performed in Refs. 31–36. The iterative local updating scheme of van Leeuwen and Baerends (LB)[37] has been used to get the KS solution. We note that a difficulty arises in the construction of accurate KS potentials from CI densities as a consequence of the wrong asymptotic behavior of the density. The Gaussian basis functions generate a Gaussian type of decay of the density, which will cause the KS potential that exactly reproduces that density to have the typical parabolic shape of the harmonic oscillator potential in the asymptotic region, cf. Ref. 38. This makes it very difficult to fix the arbitrary overall constant in the potential, which would otherwise be possible by the requirement that the KS potential goes to zero asymptotically. In practice we wish the asymptotic behavior of the potential to be determined by the density in the outer region, where it is still described accurately by the Gaussian basis functions. We fix the constant in the potential by imposing asymptotic $-1/r$ behavior beyond this outer region. The HOMO orbital energy, which should be exactly equal to $-I_H$, may differ slightly from this target value due to these difficulties in the KS potential generation (or due to inherent residual errors of the CI densities). We achieve quite good results for the HOMO orbital energies, but we note that we estimate the accuracy of the KS orbital energies in Table I to be not better than a few hundredths of an eV.

Table I compares $-\epsilon_k$ calculated for the molecules N_2, CO, HF, H_2O, and for the atoms Be and Ne with the experimental VIPs (see Table I for the corresponding references). The table also presents the HF orbital energies ϵ_k^{HF}. We differentiate between valence levels [those that can be determined with He(I) UV photoelectron spectroscopy, i.e., IP <21.2 eV] and the deep valence and core levels. A striking feature of Table I is the close correspondence between the KS $-\epsilon_k$ values and the experimental VIPs particularly for the valence levels. A typical $-\epsilon_k$ deviation Δ is close to 0.1 eV with the smallest average $\Delta=0.02$ eV for HF and the largest $\Delta=0.18$ eV for CO.

The HF Koopmans theorem produces an order of magnitude worse estimate of VIPs. The smallest average error for the upper valence levels is $\Delta=0.97$ eV for H_2O, while the largest is $\Delta=1.45$ for N_2. For N_2 the Koopmans theorem yields the wrong ordering of ionizations predicting the twofold degenerate $1\pi_u$ orbital to be the first ionized. The KS orbital energies follow the right order of ionizations. Due to the neglect of electron relaxation in cationic states, Koopman's theorem consistently overestimates VIPs, the only exception being the abovementioned ionization from the $1\pi_u$ orbital of N_2 where the wrong ordering produces underestimation of the corresponding VIP. In contrast, the KS $-\epsilon_k$ deviations are more random, being both positive and negative (see Table I).

The agreement between $-\epsilon_k$ and I_k is less precise for the lower valence and core levels. The differences are actually of the same order of magnitude as the KLI constants w_i, being 3–4 eV for the IPs of ca. 35 eV (ionizations out of the $3\sigma/2\sigma_g$ orbitals), and ca. 20 eV for the *1s* core levels. We note that empirically we find the difference between the observed I_k and the KS $-\epsilon_k$ to be quite close to $\sqrt{\epsilon_N - \epsilon_k}$ for core levels. To the extent that the differences between the KS eigenvalues and the relaxed I_k are determined by the response potential expectation values, this behavior fits in with the same square root behavior we observed for the step heights of the response potential.[20]

The results of the calculations presented in this section support the interpretation of the KS orbital energies $-\epsilon_k$ as approximate relaxed VIPs [Eq. (1.4)]. The quality of this approximation is rather high for outer valence orbitals and it becomes the exact identity (1.1) for the HOMO. In the next section more molecules will be calculated with the model KS SAOP potential.

TABLE I. Comparison of the KS and HF orbital energies $-\epsilon_k$ (eV) with experimental vertical ionization potentials (the corresponding references are indicated in the table) for the atoms Be and Ne and the molecules N_2, CO, HF, H_2O. AAD are the average absolute differences between the KS orbital energies and the VIPs for either the upper valence levels, AAD(val), or lower valence and core levels, AAD(inner).

Atom/molecule	MO	HF $-\epsilon_k$	KS $-\epsilon_k$	Expt. I_k	$I_k+\epsilon_k$	$\sqrt{\epsilon_N-\epsilon_k}$
Be (Ref. 48)	2s	8.41	9.33	9.32	−0.01	
	1s	128.78	122.29			10.63
Ne (Refs. 48 and 49)	2p	23.14	21.55	21.56	0.01	
	2s	52.53	44.84			4.82
	1s	891.77	838.48	870.30	31.82	28.58
N_2 (Refs. 50–52)	$3\sigma_g$	17.27	15.57	15.58	0.01	
	$1\pi_u$	16.72	16.68	16.93	0.25	
	$2\sigma_u$	21.21	18.77	18.75	−0.02	
AAD(val)		1.45	0.09			
	$2\sigma_g$	40.04	33.69	37.3	3.61	4.26
	$1\sigma_u$	426.67	389.72	409.98	20.26	19.34
	$1\sigma_g$	426.76	389.76	409.98	20.22	19.34
AAD(inner)		12.07	14.70			
CO (Refs. 51–53)	5σ	15.10	14.01	14.01	0.00	
	1π	17.43	16.77	16.91	0.14	
	4σ	21.90	19.33	19.72	0.39	
AAD(val)		1.26	0.18			
	3σ	41.41	34.69	38.3	3.61	4.54
	2σ	309.13	278.83	296.21	17.38	16.27
	1σ	562.32	519.71	542.55	22.84	22.49
AAD(inner)		11.93	14.61			
HF (Refs. 52, 54, and 55)	1π	17.67	16.18	16.19	0.01	
	3σ	20.91	19.92	19.9	−0.02	
AAD(val)		1.25	0.02			
	2σ	43.55	36.76	39.6	2.84	4.54
	1σ	715.48	668.46	694.23	25.77	25.54
AAD(inner)		12.6	14.31			
H_2O (Refs. 51, 52, and 56)	$1b_1$	13.76	12.63	12.62	−0.01	
	$3a_1$	15.77	14.78	14.74	−0.04	
	$1b_2$	19.29	18.46	18.55	0.09	
AAD(val)		0.97	0.05			
	$2a_1$	36.48	30.89	32.2	1.31	4.27
	$1a_1$	559.37	516.96	539.90	22.94	22.46
AAD(inner)		11.88	12.13			

IV. ϵ_i OF THE SAOP POTENTIAL VERSUS EXPERIMENTAL VIPS

While the first VIPs I_H are routinely calculated with DFT methods within the ΔSCF approach and I_H serves as a benchmark quantity to calibrate approximate DFT functionals, few ΔSCF–DFT calculations of other VIPs have been reported.[39–41] This is, in part, due to lack of the proper theoretical justification of such calculations, which require obtaining the total electronic energy of an excited cationic state from the available ground state density functionals. As was found in Ref. 41, the quality of the ΔSCF calculations of I_k with standard generalized gradient approximation (GGA) functionals is not uniform for different types of molecules (examples of larger ΔSCF–GGA errors will be considered below).

The theoretical arguments of Sec. II and the results of the accurate calculations in Sec. III suggest an alternative estimate of VIPs through the $-\epsilon_k$ of an approximate potential, which properly models the exact KS potential. It is well known, however, that standard xc potentials, obtained either from the local density approximation (LDA) or from some GGA, are not attractive enough, so that the corresponding ϵ_k are too high lying.[37] In the earlier $X\alpha$ theory[42] there were estimates of VIPs with $-\epsilon_k$ of the $X\alpha$ potential $-\alpha V_X$, where V_X is proportional to $\rho^{1/3}$, with $\alpha=1.0$. It is interesting to note that this implies ignoring the response part of the potential, which for the electron gas exchange functional just amounts to the repulsive contribution of $+0.3333V_X$, which would bring α to its Kohn–Sham–Gaspar value of 2/3.

In this section VIPs are estimated with the $-\epsilon_k$ of the orbital-dependent SAOP approximation $v_{\mathrm{xc}}^{\mathrm{SAOP}}$ (Refs. 21–23) to the accurate KS xc potential v_{xc}. Within the statistical averaging of SAOP, for core and inner valence orbitals the GLLB potential $v_{\mathrm{xc}}^{\mathrm{GLLB}}$ (Refs. 20 and 43) is used that correctly reproduces the atomic shell structure in the inner regions, while in the outer valence region the modified LB potential $v_{\mathrm{xc}}^{\mathrm{LB}\alpha}$ (Ref. 37) is employed, which reproduces the correct long-range Coulombic asymptotics of v_{xc}. The statistical averaging makes the resulting potential $v_{\mathrm{xc}}^{\mathrm{SAOP}}$ close to $v_{\mathrm{xc}}^{\mathrm{GLLB}}$ in the inner region and close to $v_{\mathrm{xc}}^{\mathrm{LB}\alpha}$ in the outer region, thus providing a balanced approximation to v_{xc} in all regions.

TABLE II. Comparison of the SAOP orbital energies $-\epsilon_k$ (eV) with experimental vertical ionization potentials for perhalo molecules. Comparing ϵ_k to $-I_k$, the deviation $\epsilon_k-(-I_k)$ is positive when the KS level is too high lying compared to $-I_k$.

Molecule	MO	Expt. VIP	$-\epsilon_k$ SAOP	Deviation
SF_6 (Ref. 57)	$1t_{1g}$	15.7	16.44	+0.74
	$1t_{2u}$	17.0	17.48	+0.48
	$5t_{1u}$	17.0	17.64	+0.64
	$3e_g$	18.6	19.28	+0.68
	$1t_{2g}$	19.8	19.83	+0.03
	$4t_{1u}^{*}$	22.6	22.47	−0.13
	$5a_{1g}$	26.85	26.07	−0.78
av. (max.) diff.				0.50 (0.74)
C_2F_4 (Ref. 58)	$2b_{3u}$	10.69	11.30	+0.61
	$4b_{3g}$	15.9	15.79	−0.11
	$6a_g$	16.6	16.21	−0.39
	$4b_{2u}$	16.6	16.26	−0.34
	$1a_u$	16.6	16.42	−0.18
	$1b_{1g}$	16.6	16.56	−0.04
	$5b_{1u}$	17.6	17.09	−0.51
	$1b_{2g}$	18.2	17.79	−0.41
	$3b_{3g}^{*}$	19.4	19.20	−0.20
	$1b_{3u}^{*}$	19.4	18.83	−0.57
	$3b_{2u}^{*}$	21.0	20.28	−0.72
	$5a_g^{*}$	21.0	20.38	−0.62
av. (max.) diff.				0.39 (0.72)
CF_4 (Ref. 58)	$1t_1$	16.2	16.60	+0.40
	$4t_2$	17.4	17.78	+0.38
	$1e$	18.5	18.35	−0.15
	$3t_2^{*}$	22.1	21.76	−0.34
	$4a_1$	25.1	24.10	−1.00
av. (max.) diff.				0.45 (1.00)
SiF_4 (Ref. 57)	$1t_1$	16.4	16.77	+0.37
	$5t_2$	17.5	17.68	+0.18
	$1e$	18.1	17.88	−0.22
	$4t_2^{*}$	19.5	19.17	−0.33
	$5a_1$	21.55	20.80	−0.75
av. (max.) diff.				0.37 (0.75)
CCl_4 (Ref. 59)	$2t_1$	11.69	12.04	+0.35
	$7t_2$	12.44	12.97	+0.53
	$2e$	13.37	13.60	+0.23
	$6t_2^{*}$	16.6	16.93	+0.33
	$6a_1$	19.9	20.11	+0.21
av. (max.) diff.				0.33 (0.53)
$CFCl_3$ (Ref. 60)	$2a_2$	11.73	12.15	+0.42
	$10e$	12.13	12.54	+0.41
	$9e^{*}$	12.97	13.34	+0.37
	$11a_1$	13.45	13.63	+0.18
	$8e^{*}$	15.05	15.37	+0.32
	$7e^{*}$	18.0	18.17	+0.17
	$10a_{a1}^{*}$	18.4	18.56	+0.16
	$9a_1^{*}$	21.5	21.32	−0.18
av. (max.) diff.				0.28 (0.42)
$CClF_3$ (Ref. 60)	$7e$	13.08	13.27	+0.19
	$10a_1$	15.20	15.56	+0.36
	$1a_2$	15.80	15.97	+0.17
	$6e^{*}$	16.72	16.64	−0.08
	$5e^{*}$	17.71	17.52	−0.19
	$9a_1^{*}$	20.20	19.69	−0.51
	$4e^{*}$	21.2	20.79	−0.41
	$8a_1$	23.8	22.97	−0.83
av. (max.) diff.				0.34 (0.83)
CCl_2F_2 (Ref. 60)	$8b_2$	12.26	12.61	+0.35
	$6b_1$	12.53	13.39	+0.86
	$3a_2$	13.11	12.91	−0.20
	$12a_1$	13.45	13.74	+0.29
	$7b_2^{*}$	14.36	14.89	+0.53
	$5b_1^{*}$	15.9	16.00	+0.10
	$2a_2^{*}$	16.30	16.45	+0.15
	$11a_1^{*}$	16.9	16.64	−0.26
	$6b_2^{*\#}$	19.3	18.86	−0.44
	$10a_1^{*}$	19.3	19.01	−0.29
	$4b_1^{*\#}$	20.4	19.99	−0.41
	$9a_1^{*}$	22.4	22.07	−0.33
av. (max.) diff.				0.35 (0.86)
$CBrF_3$ (Ref. 61)	$10e$	12.08	12.27	+0.19
	$13a_1$	14.28	14.72	+0.44
	$1a_2$	15.86	15.80	−0.06
	$9e^{*}$	16.55	16.44	−0.11
	$8e^{*}$	17.57	17.31	−0.26
	$12a_1^{*}$	19.8	19.29	−0.51
	$7e^{*}$	20.9	20.53	−0.37
	$11a_1^{*}$	23.7	22.67	−1.03
av. (max.) diff.				0.37 (1.03)
$Cl_2C{=}CF_2$ (Ref. 62)	$4b_1$	9.82	10.63	+0.81
	$11b_2$	12.13	12.34	+0.21
	$3a_2$	12.54	12.73	+0.19
	$14a_1$	12.92	13.03	+0.11
	$3b_1^{*}$	14.46	14.63	+0.17
	$10b_2^{*}$	15.54	15.66	+0.12
	$13a_1^{*}$	16.26	16.13	−0.13
	$9b_2^{*\#}$	16.26	16.34	+0.08
	$2a_2^{*}$	16.26	16.36	+0.10
	$12a_1^{*\#}$	18.18	17.99	−0.19
	$2b_1^{*}$	18.18	18.27	+0.09
	$8b_2^{*}$	20.1	19.67	−0.43
av. (max.) diff.				0.22 (0.81)
total for Table II				0.35 (1.03)

[#] New assignment based on this work.

*Higher (than the first) IP of this symmetry.

Tables II–V compare the SAOP $-\epsilon_k$ calculated for 64 molecules of various types with 406 VIPs above 27 eV obtained with photoelectron spectroscopy. Table II collects the data for 10 perhalo molecules, Table III lists 21 linear molecules, Table IV includes 19 planar molecules, and Table V includes 14 nonplanar molecules. The SAOP calculations have been performed with the Amsterdam Density Functional program (ADF).[44] The experimental geometry[45,46] and the standard ADF basis IV have been used.

The results of the SAOP calculations support the interpretation of the KS orbital energies as approximate VIPs. The main feature is the uniform reasonable quality, with which the SAOP $-\epsilon_k$ reproduce I_k for the various types of molecules. The average absolute deviations Δ are around 0.4 eV for all four types of molecules presented (see Table VI). As a matter of fact, the least $\Delta=0.35$ eV is found for perhalo molecules (Table II), for which the ΔSCF–GGA calculations produce the largest errors.[41] For example, for the molecules CF_4, CCl_4, C_2F_4, SF_6 the average ΔSCF–GGA errors are 1.94, 1.05, 1.67, and 2.19 eV, respectively.[41] The corresponding SAOP deviations are only 0.45, 0.33, 0.39, 0.50 eV, respectively, i.e., 3 to 4 times as small. Examples of the smallest and largest SAOP deviations are presented in Table III for the cyanide-substituted molecules. For HCN and FCN the

TABLE III. Comparison of the SAOP orbital energies $-\epsilon_k$ (eV) with experimental vertical ionization potentials for linear molecules.

Molecule	MO	Expt.	SAOP	Deviation	Molecule	MO	Expt.	SAOP	Deviation
HCN (Ref. 63)	1π	13.61	13.63	+0.02		$6\sigma_g$	17.8	17.89	+0.09
	5σ	14.01	13.87	−0.14		$4\sigma_u^*$	21.9	22.08	+0.18
	$4\sigma^*$	19.86	19.75	−0.11		$5\sigma_g^*$	25.6	25.19	−0.41
av. (max.) diff.				0.09(0.14)	av. (max.) diff.				0.56(1.16)
C_2H_2 (Ref. 64)	$1\pi_u$	11.49	11.41	−0.08	OCS (Ref. 67)	2π	11.24	11.83	+0.59
	$3\sigma_g$	16.7	16.40	−0.30		$1\pi^*$	15.53	16.17	+0.64
	$2\sigma_u$	18.7	18.35	−0.35		4σ	16.04	15.99	−0.05
	$2\sigma_g^*$	23.5	22.98	−0.52		$3\sigma^*$	17.96	18.00	+0.04
av. (max.) diff.				0.31(0.52)	av. (max.) diff.				0.33(0.64)
HCCF (Ref. 58)	2π	11.5	11.49	−0.01	FCN (Ref. 68)	2π	13.65	13.64	−0.01
	$1\pi^*$	18.0	17.63	−0.37		7σ	14.56	14.51	−0.05
	7σ	18.0	17.54	−0.46		$1\pi^*$	19.3	19.22	−0.08
	$6\sigma^*$	21.2	20.52	−0.68		$6\sigma^*$	22.6	22.36	−0.24
	$5\sigma^*$	24.3	23.63	−0.67	av. (max.) diff.				0.10(0.24)
av. (max.) diff.				0.55(0.68)	N_2 (Ref. 50)	$3\sigma_g$	15.58	15.24	−0.34
HCCCN (Ref. 65)	2π	11.75	12.28	+0.53		$1\pi_u$	16.93	16.44	−0.49
	9σ	13.54	13.87	+0.33		$2\sigma_u$	18.75	18.54	−0.21
	$1\pi^*$	14.18	14.45	+0.27	av. (max.) diff.				0.35(0.49)
	$8\sigma^*$	18.3	18.32	+0.02	HCCCCH (Ref. 64)	$1\pi_g$	10.30	10.75	+0.45
	$7\sigma^*$	21.3	21.41	+0.11		$1\pi_u$	12.71	12.94	+0.23
	$6\sigma^*$	25.0	24.78	−0.22		$5\sigma_g$	17.0	16.88	−0.12
av. (max.) diff.				0.25(0.53)		$4\sigma_u$	17.5	17.62	+0.12
NNO (Ref. 53)	2π	12.89	13.48	+0.59		$4\sigma_g^*$	20.0	19.87	−0.13
	7σ	16.38	16.57	+0.19		$3\sigma_u^*$	23.3	22.84	−0.46
	$1\pi^*$	18.23	18.86	+0.63		$3\sigma_g^*$	25.0	24.23	−0.77
	$6\sigma^*$	20.11	20.03	−0.08	av. (max.) diff.				0.33(0.77)
av. (max.) diff.				0.37(0.63)	HCL (Ref. 59)	2π	12.77	12.39	−0.38
NCCCCN (Ref. 65)	$2\pi_u$	11.99	12.92	+0.93		5σ	16.6	16.08	−0.52
	$7\sigma_g$	13.91	14.62	+0.71		$4\sigma^*$	25.8	25.40	−0.40
	$6\sigma_u$	14.00	14.67	+0.67	av. (max.) diff.				0.43(0.52)
	$1\pi_g$	14.16	14.75	+0.59	HF (Ref. 54)	1π	16.19	15.68	−0.51
	$1\pi_u^*$	15.00	15.75	+0.75		3σ	19.9	19.18	−0.72
	$6\sigma_g^*$	20.8	21.06	+0.26	av. (max.) diff.				0.62(0.72)
	$5\sigma_u^*$	23.0	23.27	+0.27	F_2 (Ref. 58)	$1\pi_g$	15.87	15.80	−0.07
av. (max.) diff.				0.60(0.93)		$1\pi_u$	18.8	19.04	+0.24
C_2N_2 (Ref. 65)	$1\pi_g$	13.51	14.02	+0.51		$3\sigma_g$	21.1	21.29	+0.19
	$5\sigma_g$	14.49	14.89	+0.40	av. (max.) diff.				0.17(0.24)
	$4\sigma_u$	14.86	15.28	+0.42	SiO (Ref. 69)	7σ	11.61	11.39	−0.22
	$1\pi_u$	15.6	15.90	+0.30		2π	12.19	12.17	−0.02
	$4\sigma_g^*$	22.8	23.33	+0.53		$6\sigma^*$	14.80	14.53	−0.27
av. (max.) diff.				0.43(0.53)	av. (max.) diff.				0.17(0.24)
CO (Ref. 53)	5σ	14.01	13.74	−0.27	CS (Ref. 70)	7σ	11.34	11.47	+0.13
	1π	16.91	16.53	−0.38		2π	12.90	12.86	−0.04
	$4\sigma_g^*$	19.72	18.97	−0.75		$6\sigma^*$	18.03	17.04	−0.99
av. (max.) diff.				0.47(0.75)	av. (max.) diff.				0.39(0.99)
CO_2 (Ref. 53)	$1\pi_g$	13.79	14.42	+0.63	P_2 (Ref. 71)	$2\pi_u$	10.65	10.70	+0.05
	$1\pi_u$	17.60	17.87	+0.27		$5\sigma_g$	10.84	10.87	+0.03
	$3\sigma_u$	18.08	17.90	−0.18	av. (max.) diff.				0.04(0.05)
	$4\sigma_g$	19.40	19.07	−0.33	HCCCCCN (Ref. 72)	3π	10.57	11.58	+1.01
av. (max.) diff.				0.35(0.63)		$2\pi^*$	12.70	13.50	+0.80
C_3O_2 (Ref. 66)	$2\pi_u$	10.8	11.96	+1.16		13σ	13.28	13.82	+0.54
	$1\pi_g$	15.0	16.10	+1.10		$1\pi^*$	13.96	14.65	+0.69
	$1\pi_u^*$	16.0	16.66	+0.66	av. (max.) diff.				0.76(1.01)
	$5\sigma_u$	17.3	17.65	+0.35	Total for Table III				0.40(1.39)

*Higher (than the first) IP of this symmetry.

average differences between $-\epsilon_k$ and I_k are only 0.09 and 0.10 eV, respectively, while for HCCCCCN $\Delta = 0.76$ eV is obtained.

Comparison of $-\epsilon_k$ obtained with the SAOP (Tables III and IV) and accurate KS (Table I) potentials shows that by improving further the present SAOP model one can hope to improve the agreement between the calculated $-\epsilon_k$ and VIPs. Indeed, for the molecules N_2, CO, HF, H_2O the $-\epsilon_k$ of the accurate KS potential are consistently in better agreement with VIPs than the SAOP $-\epsilon_k$. For these molecules SAOP has the KS one-electron levels listed in Table III too high compared to both the ϵ_k of the accurate potential and the experimental $-I_k$. In the general case, however, the prevailing trend is that SAOP has the highest orbitals too low lying,

TABLE IV. Comparison of the SAOP orbital energies $-\epsilon_k$ (eV) with experimental vertical ionization potentials for planar molecules.

Molecule	MO	Expt.	SAOP	Deviation
H_2CO (Ref. 73)	$2b_2$	10.9	11.05	+0.15
	$1b_1$	14.5	14.57	+0.07
	$5a_1$	16.1	15.59	−0.51
	$1b_2$*	17.0	16.68	−0.32
	$4a_1$*	21.4	20.26	−1.14
av. (max.) diff.				0.44(1.14)
H_2O (Ref. 56)	$1b_1$	12.62	12.37	−0.25
	$3a_1$	14.74	14.31	−0.43
	$1b_2$	18.55	17.95	−0.60
av. (max.) diff.				0.43(0.60)
C_2H_4 (Ref. 64)	$1b_{3u}$	10.68	10.90	+0.22
	$1b_{3g}$	12.8	12.77	−0.03
	$3a_g$	14.8	14.30	−0.50
	$1b_{2u}$	16.0	15.65	−0.35
	$2b_{1u}$	19.1	18.48	−0.62
	$2a_g$*	23.6	23.05	−0.55
av. (max.) diff.				0.38(0.62)
H_2CS (Ref. 74)	$3b_2$	9.38	9.46	+0.08
	$2b_1$	11.76	11.99	+0.23
	$7a_1$	13.85	13.67	−0.18
	$2b_2$*	15.20	15.44	+0.24
	$6a_1$*	19.9	18.87	−1.03
av. (max.) diff.				0.35(1.03)
$HCONH_2$ (Ref. 68)	$10a_1'$	10.4	10.77	+0.37
	$2a''$	10.7	11.42	+0.72
	$1a''$*	14.1	14.52	+0.42
	$9a_1'$*	14.8	15.59	−0.21
	$8a_1'$*	16.3	16.39	+0.09
	$7a_1'$*	18.8	18.35	−0.45
	$6a_1'$*	20.7	20.12	−0.58
av. (max.) diff.				0.41(0.72)
Furan (Ref. 57)	$1a_2$	9.0	9.67	+0.67
	$2b_1$	10.4	10.99	+0.59
	$9a_1$	13.0	13.14	+0.14
	$8a_1$*	13.8	13.77	−0.03
	$6b_2$	14.4	13.96	−0.44
	$5b_2$*	15.25	14.96	−0.29
	$1b_1$*	15.6	15.17	−0.43
	$7a_1$*	17.5	17.40	−0.10
	$6a_1$*	18.80	18.12	−0.68
	$4b_2$*	19.7	18.86	−0.84
	$3b_2$*	23	22.55	−0.45
av. (max.) diff.				0.42(0.84)
Thiophene (Ref. 57)	$1a_2$	8.87	9.74	+0.87
	$3b_1$	9.52	10.17	+0.65
	$11a_1$	12.1	12.33	+0.23
	$2b_1$*	12.7	13.31	+0.61
	$7b_2$	13.3	13.52	+0.22
	$10a_1$*	13.9	13.41	−0.49
	$6b_2$*	14.3	14.09	−0.21
	$9a_1$*	16.6	16.60	0.00
	$5b_2$*	17.6	17.68	+0.08
	$8a_1$*	18.3	17.90	−0.40
av. (max.) diff.				0.38(0.87)
Acrolein (Ref. 73)	$13a'$	10.1	10.65	+0.55
	$2a''$	11.0	11.76	+0.76
	$1a''$*	13.8	14.36	+0.56
	$12a'$*	13.8	13.96	+0.16
	$11a'$*	14.8	14.63	−0.17
	$10a'$*	16.2	16.04	−0.16
	$9a'$*	16.2	16.11	−0.09
	$8a'$*	18.8	18.55	−0.25
	$7a'$*	20.9	20.50	−0.40
	$6a'$*	24.6	24.45	−0.15
av. (max.) diff.				0.33(0.76)
HCOOH (Ref. 73)	$10a'$	11.5	11.87	+0.37
	$2a''$	12.6	13.09	+0.49
	$9a'$*	14.8	14.78	−0.02
	$1a''$*	15.8	15.93	+0.13
	$8a'$*	17.1	16.92	−0.18
	$7a'$*	17.8	17.61	−0.19
	$6a'$*	22.0	21.32	−0.68
av. (max.) diff.				0.29(0.68)
NSF (Ref. 75)	$13a'$	11.82	12.33	+0.51
	$12a'$*	13.50	13.75	+0.25
	$3a''$	13.87	14.24	+0.37
	$11a'$*	15.62	16.06	+0.45
	$2a''$*	16.47	16.81	+0.34
	$10a'$*#	17.2	17.17	−0.03
av. (max.) diff.				0.33(0.51)
$H_2C{=}CCl_2$ (Ref. 62)	$3b_1$	9.99	10.70	+0.71
	$8b_2$	11.69	11.84	+0.15
	$2a_2$	12.20	12.35	+0.15
	$11a_1$	12.54	12.64	+0.10
	$7b_2$*	13.80	14.21	+0.41
	$2b_1$*	14.22	14.40	+0.18
	$10a_1$*	15.93	15.85	−0.08
	$6b_2$*	16.25	16.55	+0.30
	$9a_1$*	18.51	18.43	−0.08
av. (max.) diff.				0.24(0.71)
Pyridine (Ref. 76)	$1a_2$	9.60	10.72	+1.12
	$11a_1$	9.75	10.22	+0.47
	$2b_1$	10.51	11.36	+0.85
	$7b_2$	12.61	12.90	+0.29
	$1b_1$*	13.1	13.97	+0.87
	$10a_1$*	13.8	13.95	+0.15
	$6b_2$*	14.5	14.56	+0.06
	$9a_1$*	15.9	15.67	−0.23
	$5b_2$*	15.9	15.87	−0.03
	$8a_1$*	17.4	17.16	−0.24
	$4b_2$*	19.8	19.73	−0.07
	$7a_1$*	20.6	19.72	−0.88
	$3b_2$*	23.4	23.09	−0.31
	$6a_1$*	24.5	24.22	−0.28
	$5a_1$*	28.0	27.71	−0.29
av. (max.) diff.				0.41(1.12)
s-tetrazine (Refs. 77 and 78)	$3b_{3g}$	9.72	10.24	+0.52
	$5b_{1u}$	12.05	12.54	+0.49
	$1b_{2g}$	12.05	13.01	+0.96
	$6a_g$	12.78	13.05	+0.27
	$4b_{2u}$	13.36	13.39	+0.03
	$1b_{1g}$	13.5	14.12	+0.62
	$1b_{3u}$	15.85	16.55	+0.70
	$4b_{1u}$*	16.9	17.05	+0.15
	$5a_g$*	17.6	17.71	+0.11
av. (max.) diff.				0.43(0.96)
Ozone (Ref. 79)	$6a_1$	12.73	13.26	+0.53
	$4b_2$	13.00	13.45	+0.45
	$1a_2$	13.54	14.34	+0.80
	$1b_1$	19.99	19.63	−0.36
av. (max.) diff.				0.54(0.80)
$CHF{=}CF_2$ (Ref. 58)	$4a''$	10.62	11.01	+0.39
	$16a'$	14.7	14.52	−0.18
	$15a'$*	16.0	15.78	−0.22
	$3a''$*	16.5	16.28	−0.22
	$2a''$*	16.8	16.46	−0.34
	$14a'$*	16.8	16.37	−0.43
	$13a'$*	18.0	17.61	−0.39
	$1a''$*	18.7	18.18	−0.52
	$12a'$*	20.1	19.09	−1.01
	$11a'$*	20.1	19.71	−0.39

TABLE IV. (*Continued.*)

Molecule	MO	Expt.	SAOP	Deviation
	$10a'^*$	21.9	21.09	−0.81
	$9a'^*$	25.8	24.43	−1.37
av. (max.) diff.				0.52 (1.37)
$\mathrm{CH_2{=}CF_2}$ (Ref. 58)	$2b_1$	10.70	10.97	+0.27
	$5b_2$	14.9	14.71	−0.19
	$8a_1$	15.8	15.28	−0.52
	$4b_2^*$	16.1	15.73	0.37
	$1a_2$	16.1	15.98	−0.12
	$7a_1^*$	18.2	17.48	−0.72
	$1b_1^*$	18.2	17.82	−0.38
	$3b_2^*$	19.7	19.29	−0.41
	$6a_1^*$	21.5	20.73	−0.77
	$5a_1^*$	25.2	23.98	−1.22
av. (max.) diff.				0.50 (1.22)
cis-CHF=CHF (Ref. 58)	$2b_1$	10.62	11.00	+0.38
	$7a_1$	14.0	13.88	−0.12
	$6b_2$	14.9	14.71	−0.19
	$1a_2$	16.2	15.97	−0.23
	$1b_1^*$	17.1	16.66	−0.44
	$5b_2^*$	17.1	16.65	−0.45
	$6a_1^*$	18.8	18.08	−0.72
	$5a_1^*$	18.8	18.39	−0.41
	$4b_2^*$	20.9	20.17	−0.73
	$4a_1^*$	25.2	24.03	−1.17
av. (max.) diff.				0.48 (1.17)
HCCCHO (Ref. 73)	$12a'$	10.8	11.25	+0.45
	$2a''$	11.6	12.11	+0.51
	$11a'^*$	11.7	11.97	+0.27
	$1a''^*$	14.4	14.84	+0.44
	$10a'^*$	15.9	15.71	−0.19
	$9a'^*$	17.2	17.33	+0.13
	$8a'^*$	18.4	18.44	+0.04
	$7a'^*$	21.8	21.48	−0.32
	$6a'^*$	24	24.10	+0.10
av. (max.) diff.				0.27 (0.45)
$\mathrm{HCONH_2}$ (Ref. 68)	$10a'$	10.4	10.78	+0.38
	$2a''$	10.7	11.42	+0.72
	$1a''^*$	14.1	14.53	+0.43
	$9a'^*$	14.8	14.60	−0.20
	$8a'^*$	16.3	16.36	+0.06
	$7a'^*$	18.8	18.39	−0.41
	$6a'^*$	20.7	20.11	−0.59
av. (max.) diff.				0.40 (0.72)
Total for Table IV				0.40 (1.37)

[#] New assignment based on Ref. 80.

*Higher (than the first) IP of this symmetry.

while it puts the lower levels not deep enough. Comparing ϵ_k to $-I_k$, i.e., defining the error as $-I_k-\epsilon_k$, the positive-SAOP error for the first VIPs decreases with increasing VIP, passes through zero and turns to a negative error which increases for higher VIPs. An inevitable conclusion is that the SAOP xc potential is too attractive in the outer region, since the highest orbital energies should be very close to (for the HOMO: equal to) the corresponding VIPs. For the inner region SAOP may not be attractive enough, although this cannot firmly be concluded since we should expect a negative error (i.e., too high lying level) as this occurs for the exact KS potential.

The above-mentioned trend can be clearly seen from Table VII, which collects the largest deviations of the SAOP ϵ_k from the $-I_k$. The corresponding MOs could be subdivided into two groups. The largest positive deviations are for the HOMOs of the extended systems, such as pyridine and HCCCCCN, while the largest negative deviations are for inner-valence MOs, for which the corresponding VIPs are typically higher than 20 eV. For the former group, with the exact property (1.1) in mind, one should improve the agreement between $-\epsilon_k$ and VIPs with a refined approximation to the exact KS potential. For the latter group the SAOP deviations might be, partially, due to the expected underestimation of VIPs by $-\epsilon_k$ for the inner orbitals, due to the v_{resp} matrix elements, as has been discussed in Sec. III.

V. CONCLUSIONS

The physical meaning of the KS orbital energies has remained a matter of concern until recently.[15,47] In this paper we have shown that the KS orbital energies $-\epsilon_k$ approximate very well *relaxed* vertical ionization potentials I_k. Exact relations between ϵ_k and I_k are established with a set of linear equations for the ϵ_k, which are expressed through I_k and the matrix elements $\epsilon_k^{\mathrm{resp}}$ of the response potential v_{resp}. Although $-I_k$ will be a leading contribution to ϵ_k, other $I_{j\neq k}$ do enter through coupling terms which are determined by the overlaps between the densities of the KS orbitals as well as by overlaps between the KS and Dyson orbital densities.

The orbital energies of accurate KS solutions obtained from *ab initio* densities are compared with the experimental VIPs of the molecules N_2, CO, HF, H_2O. Very good agreement between the accurate $-\epsilon_k$ of the outer valence KS orbitals and the corresponding VIPs is established, with the average difference approaching 0.1 eV. This agreement is much better than for HF or exact exchange KS orbital energies. The lower valence KS levels are a few eV higher than the corresponding $-I_k$, and the core levels some 20 eV, in agreement with the theoretically deduced up-shift of the KS levels compared to $-I_k$ by the response potential matrix elements. Furthermore, ϵ_k values are calculated for 64 molecules of various types with the approximate KS SAOP potential and they are compared with 406 experimental VIPs. Reasonable agreement between the SAOP $-\epsilon_k$ and the outer valence VIPs is found with an average deviation of about 0.4 eV.

The present results provide more physical meaning for the Kohn–Sham approach of DFT and they counter the standard view, that the KS orbitals and their energies are merely auxiliary quantities which, in general, have no definite physical meaning. We have demonstrated that, to the contrary, while Koopman's theorem interprets the HF orbital energies $-\epsilon_k^{\mathrm{HF}}$ as *unrelaxed* VIPs, the KS $-\epsilon_k$ can be interpreted as approximate *relaxed* VIPs I_k. The quality of this approximation appears to be high for outer valence orbitals and it becomes an exact identity for the HOMO. Similarly, while the HF orbitals are interpreted as the unrelaxed Dyson orbitals, the KS outer valence orbitals can be interpreted as approximate relaxed Dyson orbitals, which agrees with recent results for the correspondence between KS and Dyson orbitals of Koren *et al.*[30] Our present results complement similar results concerning the nature and meaning of the KS orbitals themselves.[2–5,24] The relations (2.27) between ϵ_k and I_k, since they interestingly involve both KS and Dyson orbitals,

TABLE V. Comparison of the SAOP orbital energies $-\epsilon_k$ (eV) with experimental vertical ionization potentials for nonplanar molecules.

Molecule	MO	Expt.	SAOP	Deviation
CH_3COCH_3 (Ref. 57)	$5b_2$	9.8	10.23	+0.43
	$2b_1$	12.6	12.93	+0.33
	$4b_2$*	13.4	13.35	−0.05
	$8a_1$	14.1	13.82	−0.28
	$1a_2$	14.4	14.23	−0.17
	$7a_1$*	15.7	15.27	−0.43
	$3b_2$*	15.7	15.51	−0.19
	$1b_1$*	16.0	15.66	−0.34
	$6a_1$*	18.0	17.44	−0.56
	$5a_1$*	24.6	23.47	−1.13
av. (max.) diff.				0.39(1.13)
NH_3 (Ref. 57)	$3a_1$	10.8	10.73	−0.07
	$1e$	16.0	15.65	−0.35
av. (max.) diff.				0.21(0.35)
CH_4 (Ref. 64)	$1t_2$	13.6	13.85	+0.25
	$2a_1$	22.9	21.50	−1.40
av. (max.) diff.				0.83(1.40)
CH_3CCH (Ref. 64)	$2e$	10.54	10.61	+0.07
	$1e$*	14.6	14.71	+0.11
	$7a_1$	15.4	15.15	−0.25
	$6a_1$*	17.4	17.12	−0.28
	$5a_1$*	22.4	21.46	−0.94
	$4a_1$*	23.9	23.50	−0.40
av. (max.) diff.				0.34(0.94)
CH_3CN (Ref. 65)	$2e$	12.46	12.58	+0.12
	$7a_1$	13.17	13.12	−0.05
	$1e$*	15.7	15.92	+0.22
	$6a_1$*	17.4	17.19	−0.21
	$5a_1$*	24.9	23.82	−1.08
av. (max.) diff.				0.34(1.08)
CH_3NC (Ref. 65)	$7a_1$	11.32	11.46	+0.13
	$2e$	12.5	12.62	+0.12
	$1e$*	16.1	16.03	−0.07
	$6a_1$*	18.2	18.02	−0.18
	$5a_1$*	25.0	23.52	−1.48
av. (max.) diff.				0.40(1.48)
CH_3F (Ref. 58)	$2e$	13.1	13.21	+0.11
	$1e$*	17.0	16.56	−0.44
	$5a_1$	17.0	16.95	−0.05
	$4a_1$*	23.4	22.05	−1.35
av. (max.) diff.				0.49(1.35)
CH_2F_2 (Ref. 58)	$2b_1$	13.3	13.45	+0.15
	$4b_2$	15.4	15.14	−0.26
	$6a_1$	15.4	15.37	−0.03
	$1a_2$	15.8	15.64	−0.16
	$3b_2$*	19.1	18.68	−0.42
	$1b_1$*	19.1	18.56	−0.54
	$5a_1$*	19.1	18.55	−0.55
	$4a_1$*	24.0	22.64	−1.36
av. (max.) diff.				0.43(1.36)
CF_3CN (Ref. 68)	$6e$	14.3	14.59	+0.29
	$10a_1$	14.3	14.80	+0.50
	$9a_1$*	16.3	17.02	+0.72
	$1a_2$	16.5	16.46	−0.04
	$5e$*	17.0	17.11	+0.11
	$4e$*	18.1	17.99	−0.11
	$3e$*	21.6	21.25	−0.35
	$8a_1$*	22.6	22.10	−0.50
	$7a_1$*	25.8	25.12	−0.68
av. (max.) diff.				0.37(0.72)
CH_3CCCN (Ref. 65)	$3e$	10.95	11.58	+0.63
	$11a_1$	13.06	13.41	+0.35
	$2e$*	13.52	13.88	+0.36
	$1e$*	15.2	15.78	+0.58
	$10a_1$*	16.5	16.51	+0.01
	$9a_1$*	20.5	20.39	−0.11
	$8a_1$*	23.7	23.18	−0.52
av. (max.) diff.				0.37(0.63)
CHF_3 (Ref. 58)	$6a_1$	14.8	15.13	+0.33
	$1a_2$	15.5	15.72	+0.22
	$5e$	16.2	16.30	+0.10
	$4e$*	17.2	17.19	−0.01
	$3e$*	20.7	20.30	−0.40
	$5a_1$*	20.7	20.41	−0.29
	$4a_1$*	24.4	23.40	−1.00
av. (max.) diff.				0.34(1.00)
NSF_3 (Ref. 81)	$7e$	12.50	13.26	+0.76
	$10a_1$	14.15	14.83	+0.68
	$1a_2$	16.65	17.02	+0.37
	$6e$*	16.65	17.43	+0.78
	$5e$*	18.35	18.59	+0.24
av. (max.) diff.				0.57(0.78)
CH_3CH_3 (Ref. 64)	$1e_g$	12.0	12.47	+0.47
	$3a_{1g}$	12.7	13.09	+0.39
	$1e_u$	15.0	14.81	−0.19
	$2a_{2u}$	20.4	19.38	−1.02
	$2a_{1g}$*	23.9	22.85	−1.05
av. (max.) diff.				0.62(1.05)
CH_3CONH_2 (Ref. 68)	$13a'$	10.0	10.44	+0.44
	$3a''$	10.4	11.05	+0.65
	$2a''$*	13.0	13.28	+0.28
	$12a'$*	14.1	13.86	−0.24
	$11a'$*	14.5	14.17	−0.33
	$10a'$*	15.4	15.76	+0.36
	$1a''$*	16.0	15.24	−0.76
	$9a'$*	18.0	17.55	−0.45
	$8a'$*	19.4	18.71	−0.69
	$7a'$*	23.9	22.51	−1.39
av. (max.) diff.				0.56(1.39)
Total for Table V				0.43(1.48)

*Higher (than the first) IP of this symmetry.

would warrant a more extensive comparative study of these orbitals and of the matrices **M** and **P**, that will provide more understanding of how the various I_k contribute to a specific KS ϵ_k.

The present work justifies what we could call the "$-\epsilon$ method," according to which the valence VIPs of a molecule can be effectively estimated as $-\epsilon_k$ with just a single calculation of the neutral ground state with a proper approxima-

TABLE VI. Summary of Tables II–V.

Table	Average abs. diff.	Maximal abs. diff.	Type of molecules
II	0.35	1.03	perhalo
III	0.38	1.16	linear
IV	0.40	1.37	planar
V	0.43	1.48	nonplanar
Total	0.39	1.48	

TABLE VII. Large absolute deviations in Tables II–V.

Molecule	MO	Deviation	Nature of MO
CH_3NC	$5a_1$	-1.48	inner-valence
CH_4	$2a_1$	-1.40	inner-valence
CH_3CONH_2	$7a'$	-1.39	inner-valence
$CHF=CF_2$	$9a'$	-1.37	inner-valence
CH_2F_2	$4a_1$	-1.36	inner-valence
CH_3F	$4a_1$	-1.35	inner-valence
$CH_2=CF_2$	$5a_1$	-1.22	inner-valence
cis-$CHF=CHF$	$4a_1$	-1.17	inner-valence
H_2CO	$4a_1$	-1.14	inner-valence
CH_3COCH_3	$5a_1$	-1.13	inner-valence
CH_3CN	$5a_1$	-1.08	inner-valence
CH_3CH_3	$2a_{1g}$	-1.05	inner-valence
H_2CS	$6a_1$	-1.03	inner-valence
$CBrF_3$	$11a_1$	-1.03	inner-valence
CH_3CH_3	$2a_{2u}$	-1.02	inner-valence
$CHF=CF_2$	$12a'$	-1.01	inner-valence
CF_4	$4a_1$	-1.00	inner-valence
CHF_3	$4a_1$	-1.00	inner-valence
CS	6σ	-0.99	inner-valence
CH_3CCH	$5a_1$	-0.94	inner-valence
OCCCO	$2\pi_u$	$+1.16$	HOMO (extended)
pyridine	$1a_2$	$+1.12$	HOMO (extended)
HCCCCCN	3π	$+1.01$	HOMO (extended)
s-tetrazine	$1b_{2g}$	$+0.96$	3rd VIP (extended)
NCCCCN	$2\pi_u$	$+0.93$	HOMO (extended)

tion to the exact KS potential. SAOP provides an example of such an approximation, with its uniform quality of the VIP estimate for various types of molecules considered. It is shown to be an efficient alternative to the ΔSCF approach with standard GGA functionals, which requires calculations of both neutral ground state and all relevant excited cationic states, and which may exhibit a nonuniform quality for various types of molecules.[41] The $-\epsilon$-SAOP method can be employed to predict and to interpret photoelectron spectra, and in this paper SAOP has been used to reassign several VIPs for the molecules CF_2Cl_2, $Cl_2C=CF_2$ (see Table II), and NSF (see Table V).

The present interpretation can serve as a basis for further development of DFT methods. It suggests, in particular, that the reliable outer valence VIPs obtained with photoelectron spectroscopy can be used as benchmark data to calibrate approximate KS xc potentials. In this paper the comparison of the SAOP $-\epsilon_k$ with the experimental VIPs leads to the conclusion, that the SAOP xc potential is too attractive in the outer region. This shows a direction for refinement of this potential.

ACKNOWLEDGMENTS

One of the authors (D.P.C.) wishes to acknowledge a visiting professorship from the Netherlands Foundation for Scientific Research (NWO), and O.V.G. also acknowledges support from NWO. E.J.B. is grateful for a Schlumberger professorship at Cambridge University.

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