What Do the Kohn−Sham Orbitals and Eigenvalues Mean?

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Abstract: Kohn−Sham orbitals and eigenvalues are calculated with gradient-corrected functionals for a set of small molecules (H_2O, N_2, CrH_6^{6-}, and $PdCl_4^{2-}$), varying basis sets and functionals. The calculated Kohn−Sham (KS) orbital shapes, symmetries, and the order and absolute energy of the associated eigenvalues are investigated and compared with those of Hartree−Fock (HF) and one-electron extended Hückel (eH) calculations, as well as experimental ionization potentials. The shape and symmetry properties of the KS orbitals are very similar to those calculated by HF and eH methods. The energy order of the occupied orbitals is in most cases in agreement among the various methods. The order of empty orbitals of a minimal basis set is sometimes interchanged, within that group or with some orbitals resulting from a larger basis calculation. Overall the KS orbitals are a good basis—as Baerends suggested—for qualitative interpretation of molecular orbitals. For the Kohn−Sham eigenvalues we find an approximately linear dependency of $|\epsilon_i^{KS} - \epsilon_i^{HF}|$ vs ϵ_i^{HF} ($\approx$−IP) for the occupied as well as for the unoccupied orbital eigenvalues. We suggest an $ax + b$ scaling for quantitative interpretation of KS eigenvalues, at least if these are calculated utilizing commonly used functionals.

1. Introduction

Chemists have found orbitals useful—atomic orbitals, molecular orbitals, the orbitals of molecular fragments. Orbitals provide a natural language for an *aufbau* of the complex reality of the molecules of the inorganic and organic world.

As Hartree−Fock self-consistent-field theory and its improvement through configuration interaction (HF-SCF and CI) evolved, the "reality" of orbitals was both strengthened and weakened. The strengthening was derived from Koopman's theorem, which provided a simple and natural connection between orbital energy and ionization potential (enhanced by the development of photoelectron spectroscopy, which effectively allowed us to measure easily ionization potentials (IP's) other than the first). However, the limitation of the single-configuration viewpoint weakened, so to speak, the reality of orbitals. If many states of a molecule are not well described by one (or two) configurations, the orbital idea loses its utility.

We are in a time of ascendency of density functional theory[1−3] for the computation of the electronic structure of molecules. The methodology contains orbitals to be sure, the Kohn−Sham (KS) orbitals[4] which we will denote as ϕ_i, with associated eigenvalues ϵ_i. But the fundamental variable, which determines all observables, is the total electron density $\sum_i \phi_i^2 = \rho$.

From the beginning of the utilization of the density functional method, the significance of the Kohn−Sham orbitals has been deemphasized, perhaps because it its very difficult to extract quantitative information from these orbitals. They have been often viewed as just an auxiliary construct, a necessary but not necessarily meaningful way to build up the all-important total density. Here then is the crux of the problem—chemists know that orbitals are useful, but the physicists and chemists who use density functional theory so fruitfully have by and large shied away from attributing to Kohn−Sham orbitals the reality that (we think) they deserve.

As with any general statement, this is an exaggeration. There are theoreticians[5−14] who *have* provided a welcome place for orbitals in the density functional scheme—Baerends[13,14] and Parr[10−12] are prominent examples. Baerends' impressive work pinpoints the physical significance of KS orbitals by "splitting the exchange-correlation part of the KS potential into a part that is directly related to the total energy and a so-called response part that is related to response of the exchange-correlation hole to density change".[13,14] Baerends and co-workers in fact argue that the KS orbitals are *very* suitable for qualitative, chemical applications. Meanwhile, without waiting for the justification that Baerends' arguments provide, the chemical community has begun—mainly in the past few years—to apply KS orbitals in rationalizing chemical phenomena,[15−22] as we are used to doing with extended Hückel (eH) orbitals.

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Table 1. Parameters Used in the EH Calculations

atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1	C_2
H	1s	−13.6	1.3			
N	2s	−26.0	1.950			
	2p	−13.4	1.950			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
Cl	3s	−26.3	2.183			
	3p	−14.2	1.733			
Cr	4s	−8.66	1.7			
	4p	−5.24	1.7			
	3d	−11.22	4.95	0.5060	1.80	0.6750
Pd	5s	−7.32	2.19			
	5p	−3.75	2.152			
	4d	−12.02	5.983	0.5535	2.613	0.6701

In this paper we confront the problem discussed above empirically and directly, we hope. We ask two questions: (1) Are the KS orbitals different in number, symmetry properties, and shape from the orbitals of a HF-SCF calculation or from those of a one-electron scheme? (2) What shall we make of the Kohn−Sham eigenvalues given by currently popular potentials? How are they related to ionization potentials? Do they provide an energy ordering of the orbitals that resembles or differs from that given by HF-SCF, one-electron schemes, or experimental IP's?[23]

2. Methodology

KS and HF-SCF calculations were performed by means of the Gaussian 94 program package.[24] For all HF and DF (functional BP86) calculations on first- and second-row molecules the 6-31G* basis set was used. For transition-metal complexes we worked with the comparable size LANL1DZ basis set with a Los Alamos ECP. For the variation of basis sets and functionals the STO-3G, 3-21G, 6-31G, 6-31G*, 6-311G, 6-311G*, 6-311G** basis sets and BHandH, X-α, BP86, BLYP, PW91, HFS, and SVWN (LDA) exchange correlation functionals were investigated. eH orbital energy values were calculated with the program YAeHMOP[25] and the parameter set given in Table 1.

We will study the following molecules in detail: H_2O, N_2, CrH_6^{6-}, and $PdCl_4^{2-}$. In case of the DF and HF calculations we perform a full geometry optimization; for the hypothetical CrH_6^{6-} we looked at single-point calculation on a MP2/double-ζ optimized O_h CrH_6 geometry.[26,27] The eH results are for the experimental geometries (H_2O,[28] N_2,[29] $PdCl_4^{2-}$[30]) and for the MP2/double-ζ optimized geometry of CrH_6.

2.1. Orbital Shape: The Case of Water. Of course, the number and symmetry properties of the KS orbitals, the canonical HF orbitals, and eH orbitals are the same for the *occupied levels* (the eH orbitals do not contain the core 1s levels). Could it be different? Could you imagine that the KS orbitals of, for example, a Ne atom are not 1s, 2s, 2p-like? One would justifiably think the eH orbitals are a poor approximation (to either the HF-SCF or DFT orbitals), but even as poor as that approximation might be, the qualitative description of the orbitals, really determined as it is by their nodal structure, should be the same.

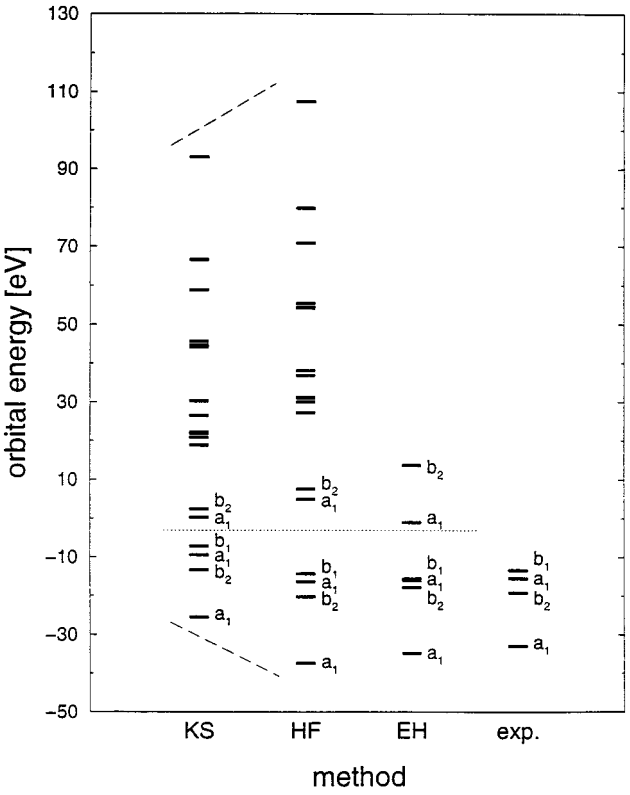

Figure 1. Calculated occupied valence and virtual orbitals for water by BP86/6-31G*, RHF/6-31G*, and eH methods, as well as the experimental values.[39] The Fermi level is indicated by a dotted line; the compression of the KS levels relative to HF levels is highlighted by dashed lines.

We need to be a little more precise, however, in defining several types of orbitals: group I, core levels (e.g. 1s on oxygen); group II, occupied valence orbitals; group III, unoccupied valence orbitals; group IV, higher unoccupied orbitals, mainly a result of the larger basis. Figure 1 shows the one-electron energies of these orbitals for eH, DFT, and HF-SCF calculations for a water molecule.

The eH calculations by definition use a valence orbital basis set; therefore, they lack group I + IV orbitals. The HF-SCF and DFT calculations have orbitals of all kinds, the number of group IV orbitals depending, of course, on this basis set size.

The border between group III and IV levels cannot be sharp. In particular, there are excited states which are reasonably well-decribed by valence-state MO's and others (e.g. Rydberg states) which need a large basis for an accurate description.

There is no doubt that each method gives (aside from the core states) for water four occupied valence energy levels of

(23) Many of these questions have been addressed by R. G. Parr and co-workers,[1,10−12] whose excellent work provides a quantitative account of the relationship between KS and HF orbitals and suggests that the EH method be viewed as a particular empiricization of the KS method.

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(26) The simplest conceivable 18-electron transition-metal complex (CrH_6^{6-}) is not stable in DF and HF geometry optimizations, presumably due to the high negative charge. To calculate this prototype, we used therefore the optimized CrH_6 geometry and did a single-point SCF calculation for the 6− species.

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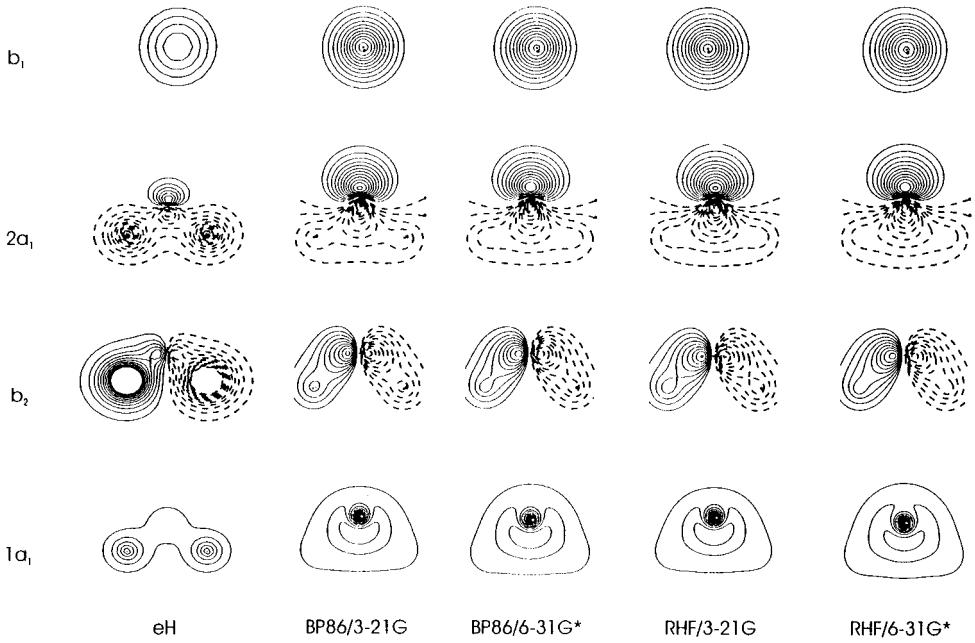

Figure 2. Calculated contour plots (*xy* plane) of the a_1, b_2, a_1, and b_1 orbitals of water (for b_1, $\Psi = 0$ in the *xy* plane; this orbital is hence plotted with an offset of 0.5 Å) with BP86/3-21G, BP86/6-31G*, RHF/3-21G, RHF/6-31G*, and eH methods.

$2a_1 + b_2 + b_1$ symmetry. We will discuss the energies of these levels and the significance of the eigenvalues in the next section; here we want to focus on their shape.

Figure 2 shows a contour diagram of the four occupied valence MO's of water computed by the three methods (two basis sets for HF-SCF and DFT).

Are these orbitals similar or different? The eH orbitals arbitrarily exclude the core and use nodeless Slater functions; thus, the eH orbitals are recognizably different, especially near the nuclei. The other four sets of orbitals are, on the scale of the figure, nearly indistinguishable (we could exaggerate the difference with a density difference map), and away from the nuclei they are not that different from the eH orbitals.

2.2. Orbital Energies and Their Ordering, and the Relationship to Ionization Potentials: Water. The general literature of density functional theory states that *only* the energy ϵ_i of the highest occupied KS orbital (HOMO) has physical significance, in the sense that the ϵ_i value of the HOMO is in theory equal to the first ionization potential[1−4,31,32] In practice, with the commonly used functionals implemented in standard quantum chemistry program packages, even HOMO energies differ significantly from experimental data (e.g. IP = 14.52 eV[35] and $\epsilon_{HOMO}^{LDA} = -6.50$ eV for the nitrogen atom[36]). This deviation arises from the insufficient cancellation of the self-interaction error in the Hartree term $\int\int d^3r_i d^3r_j[\rho(r_i)][W(r_i,r_j)]-[\rho(r_j)]$ by terms of the opposite sign in the *approximated* exchange-correlation functionals.[2] New functionals and approximations for the KS potential[37,38] have been developed (e.g. LSDSIC, OEP, KLI) which correct the self-interaction error and lead to precise agreement of the *HOMO* energy with the first IP; hopefully these approximations will be implemented in quantum chemistry packages soon.

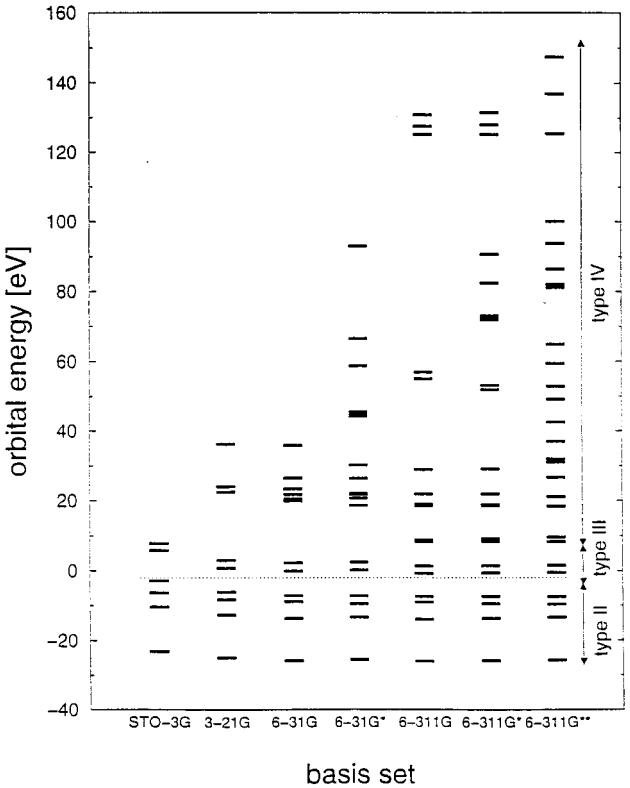

Figure 3. Calculated occupied valence and virtual KS orbitals for water using a BP86 functional but varying the basis set. The occupied core orbitals are denoted as type I, the occupied valence orbitals as type II, the virtual orbitals arising from a minimal basis as type III, and all other virtual orbitals as type IV; the Fermi level is indicated by a dotted line.

We begin our study with the influence of the basis set chosen on the KS energy levels. In Figure 3 the KS orbital energies of the water molecule, calculated with the BP86 functional and different basis sets, are shown. The absolute KS orbital energy values are (with the exception of the inadequate STO-3G

(31) The proof[33] given in 1982 that $\epsilon_{HOMO} = -IP$ has been recently questioned by Kleinman.[34]

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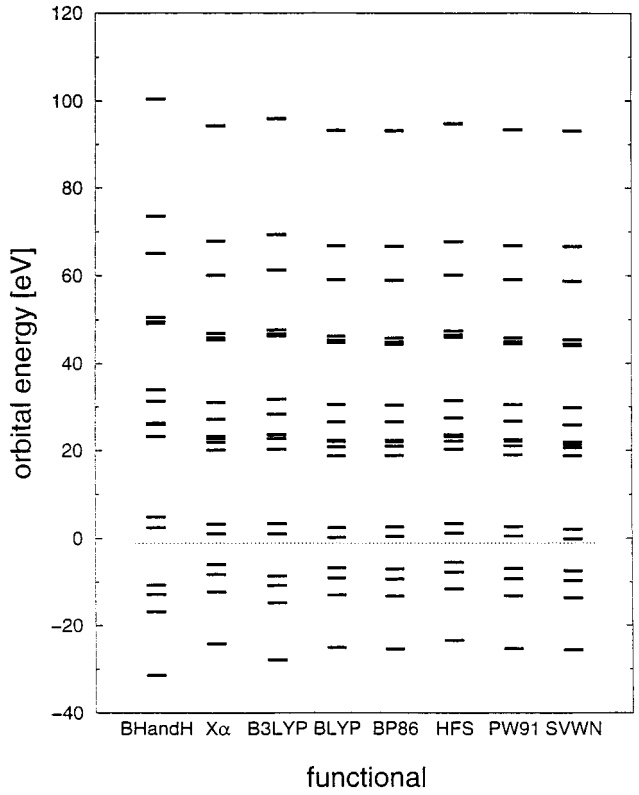

Figure 4. Calculated occupied valence and virtual orbitals for water, assuming a 6-31G* basis and varying the functional. The Fermi level is indicated by a dotted line.

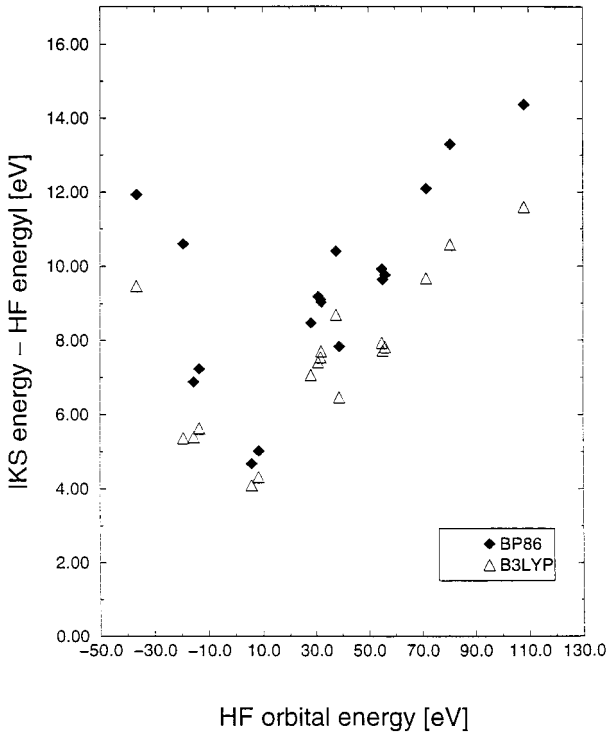

Figure 5. Differences of RHF/6-31G* and DF(BP86, B3LYP)/6-31G* calculated orbital energies plotted vs RHF/6-31G* orbital energies for water.

minimal basis set) roughly independent of the basis set for type II and III orbitals. The symmetries and order of all KS orbitals are not influenced by expanding the basis set.

Next (cf. Figure 4) we study the influence of the exchange-correlation functional used on the KS orbital energies of the water molecule. We included the BHandH, Xalpha, BP86, BLYP, PW91, HFS, and SVWN (LDA) exchange correlation functionals. The basis is fixed as a common 6-31G* set of double-ζ quality.

The KS energy levels drawn in Figure 4 show substantial absolute energy shifts, depending on the applied functional. However, the relative spacing of the levels (e.g. the HOMO−LUMO gap) is approximately constant within the entire set (except for the hybrid functionals B3LYP and BHandH). The variation in the orbital energies may be traced to different self-interaction errors of the applied functional. If the absolute shifts are corrected by a suitable scaling, e.g. by a constant energy relative to the experimentally accessible HOMO energy (as measured by the ionization potential), then the orbital energies of all examined functionals (except the hybrid functional B3LYP and the BHandH functional) match very well. However, if no scaling is applied, one has to be aware that different contemporary functionals may lead to orbital energies different by up to 10 eV from each other for a given valence orbital. A reviewer (whom we thank) aptly remarks: "The finite basis set can be arbitrarily large until its finiteness causes 'negligible' errors—given enough computing power. Improving approximate usable XC-potentials is an ongoing major theoretical challenge".

There is more to be learned from the orbital energies computed by the various methods. In Figure 1 the KS orbital energies of water (calculated with the BP86/6-31G* functional/basis set combination) were shown, along with the orbital energy levels of Hartree−Fock (RHF/6-31G*) and extended Hückel (YAeHMOP[25]) calculations and the experimentally determined vertical IP's.[39] As far as the occupied orbital energies go (cf. Figure 1; the gap between filled and unfilled levels is indicated by a dotted line), the HF results match well the experimental IP's. The eH results are in acceptable agreement with experimental data (cf. Figure 1) as well. However, the KS energy levels are shifted by a constant (e.g. for the HOMO $\Delta\epsilon \approx 7$ eV) to higher energy, relative to the HF results.

During preparation of this paper we became aware of work similar in motivation to ours, by Politzer and Abu-Awwad.[40,41] These authors examine the relationship between various IP's and the KS and HF ϵ_i's. Their results for the H_2O molecule are similar to ours, and in general they find that the calculated KS ϵ_i's differ significantly from the experimental IP's, as we do.

It must be mentioned right away here that people who use DFT calculations and are interested in IP's or ultraviolet photoelectron spectroscopy (UPS) do not generally focus on the ϵ_i's but calculate IP's as E(molecule) − E(cation radical), choosing the appropriate cation radical state. The results are in general quite satisfactory. Still, one would like to see if a "Koopman's-theorem like" association of IP's with KS ϵ_i's calculated with common functionals might work.

2.3. A Scaling Relationship. We find a systematic (if as yet mysterious) relation between KS energies, calculated with gradient corrected functionals, and IP's (which are close to the HF values). In Figure 5 we plot the energy difference between the HF and KS orbital energies vs the HF orbital energies (which are close to the IP's for the occupied levels). One can see a linear energy shift[42] for the occupied orbital energies (left part of the graph; rhomboid symbols).[43] In calculations on extended

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(42) This linear dependency is not necessarily valid for the (yet unknown) true KS eigenvalues.

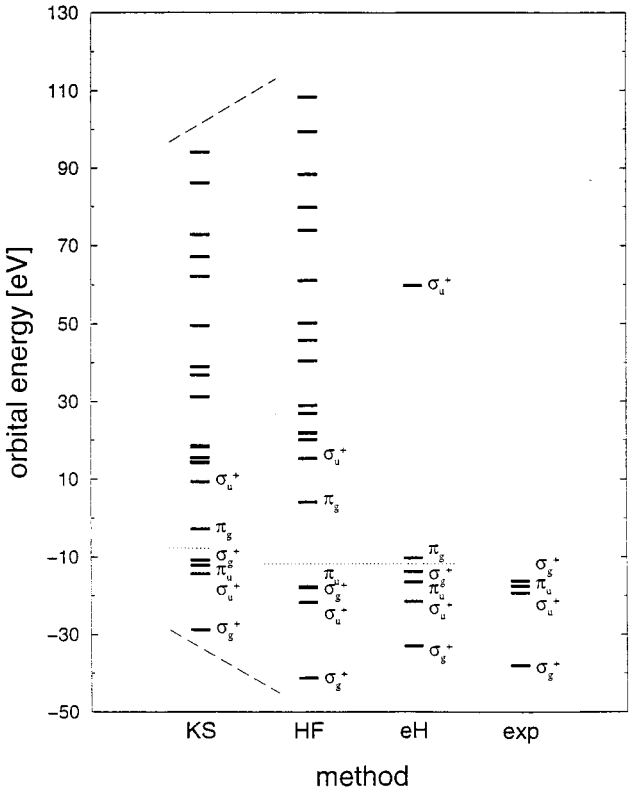

Figure 6. Calculated occupied valence and virtual orbitals for the nitrogen molecule by BP86/6-31G*, RHF/6-31G*, and eH methods and experimental values.[39] The compression of the KS levels relative to HF levels is highlighted by dashed lines.

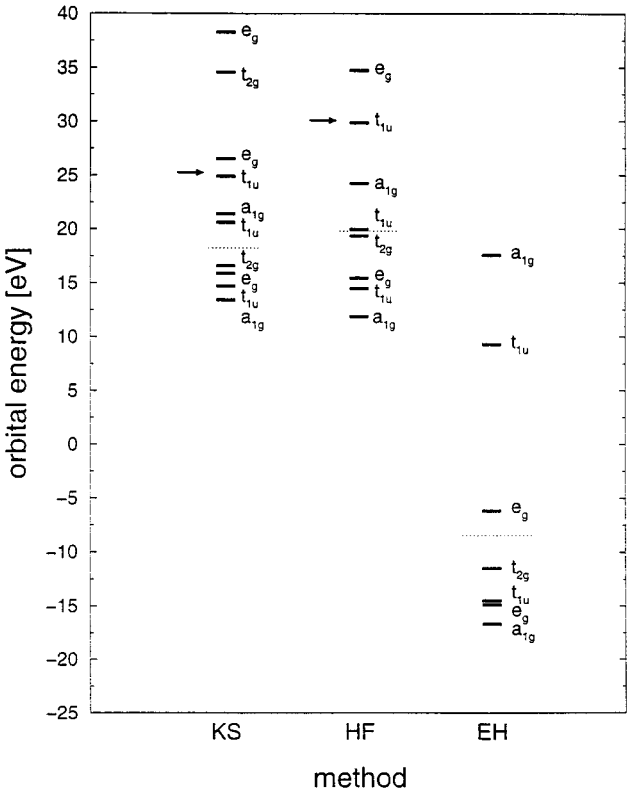

Figure 7. Calculated occupied valence and virtual orbitals for CrH_6^{6-} by BP86/LANDZL1, RHF/LANDZL1, and eH methods. The Fermi level is indicated by a dotted line.

systems similar linear dependencies between KS and so-called quasi-particle band energies appear.[44] Most intriguing in Figure 5 (right part of the graph; ◆ symbols) is that this linear energy shift apparently also applies to the virtual orbitals! This is consistent with the fact that calculated virtual KS energy levels are usually found to be of lower energy than those of HF calculations.[45−47]

To obtain a correspondence between KS (calculated with gradient-corrected functionals, e.g. BP86) and HF orbital energies, an empirical scaling of the form $ax + b$ appears to be necessary. b adjusts for the constant shift (self-interaction error), and a accounts phenomenologically for the linear scaling which we find. We defined a and b in that way that a^{occ} and a^{virt} are the slopes of the interpolation lines (cf. Figure 5) for the occupied and virtual orbital energy differences, respectively, and b is the y intercept of the crossing of the two interpolation lines. Specific calculation of a and b gives the following for H_2O: $a_{H_2O}{}^{occ} = -0.24$, $b_{H_2O} = 4.68$ eV, and $a_{H_2O}{}^{virt} = 0.15$.

The other data set in Figure 5 (symbolized by triangles) shows what transpires if ones uses the B3LYP functional. The deviation is—as one expects from the hybrid character of the functional (intermediate between HF and DFT)—smaller than that of the pure density functionals. This is in agreement with the fact that band gaps of hybrid functionals lie between the calculated DF and HF band gap energies[48] and with calculations in the literature[40] using hybrid functionals and the 6-31+G** basis set.

The calculated core orbital energy $\epsilon_{BP86}{}^{core} = -510.87$ eV of the water molecule is very different from the HF result $\epsilon_{HF}{}^{core} = 559.17$ eV. Again the HF energy represents a reasonably good reference, because the sum of the experimental determined core energy $\epsilon_{exptl}{}^{core} = 539.89$ eV[49] and an estimation of the relaxation effect $\epsilon_{relax}{}^{core} \approx 20$ eV[50] gives an energy value of ∼560 eV, which is close to the HF result. The calculated difference $\epsilon_{BP86}{}^{core} - \epsilon_{HF}{}^{core}$ lies roughly on the extrapolated line in Figure 5 ($a_{H_2O,core}{}^{occ} \approx 0.1$).

Qualitatively, the order in energy of the calculated occupied and virtual H_2O orbitals is consistent for all methods applied (cf. Figure 5). Orbitals of type IV appear above the orbitals type III.

2.4. The Case of N_2. The next molecule we want to focus on is N_2, because two of the valence orbitals of N_2, $\sigma_g{}^+(2p_z)$ and $\pi_{1u}(2p_{x,y})$, are close together in energy. Figure 6 shows trends similar to those found for the water molecule. The calculated HF orbital energies match best with the experimental values; eH one-electron energies are acceptably close, and the KS orbitals show again the $ax + b$ energy shift. Clearly one can also see this shift in the compression (indicated by dashed lines, cf. Figure 6) of the KS orbital energy spacing relative to the HF energies plotted. The calculated scaling parameters $a_{N_2}{}^{occ} = 0.27$, $b_{N_2} = 5.4$ eV, and $a_{N_2}{}^{virt}$ are relatively close to the values for the H_2O molecule.

Interestingly the experimentally determined (and very sensitive) order of highest occupied levels "π_u under $\sigma_g{}^+$"[39] is well

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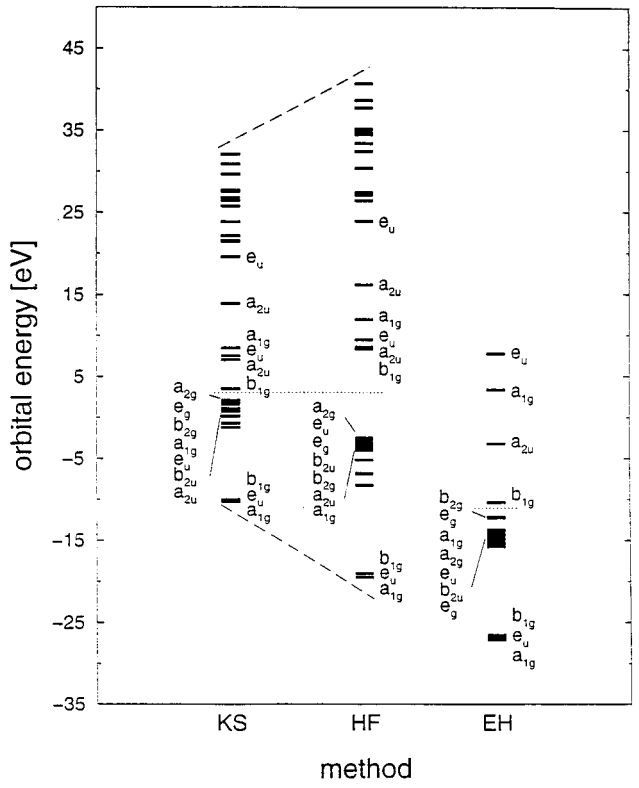

Figure 8. Calculated occupied valence and virtual orbitals for $PdCl_4^{2-}$ by BP86/LANDZL1, RHF/LANDZL1, and eH methods. The Fermi level is indicated by a dotted line. The compression of the KS levels relative to HF levels is emphasized by dashed lines.

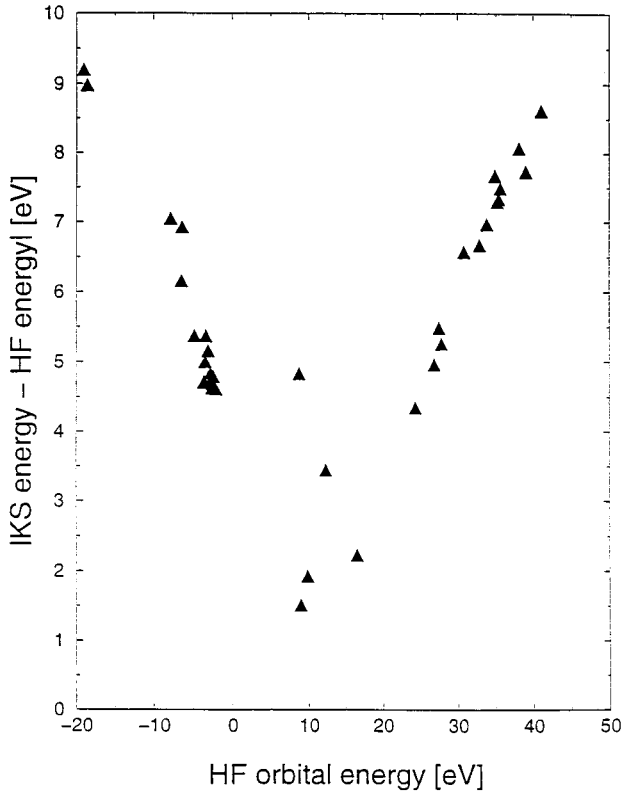

Figure 9. Differences of RHF/6-31G* and DF(BP86)/6-31G* calculated orbital energies plotted vs RHF/6-31G* orbital energies for $PdCl_4^{2-}$.

reproduced by KS as well as eH calculations. In the HF results[51] the $\pi_u - \sigma_g^+$ ordering (cf. Figure 6) is interchanged. The symmetries and shapes of the orbitals calculated with DF, HF, and eH methods are as they should be and are consistent with each other.

The same trends are observed in calculations (not reported here) on molecules such as O_2, F_2, ethane, ethylene, singlet CH_2, and triplet CH_2.

2.5. A Transition-Metal Case, CrH_6^{6-}. To study a bit more complicated orbital ordering, where energy levels of different types are still closer together, we investigated the orbital energies of the simplest conceivable 18-electron ML_6 transition-metal complex, the hypothetical d^6 CrH_6^{6-} (cf. Figure 7). For such a prototype octahedral organometallic complex, one would expect filled a_{1g}, t_{1u}, e_g levels, localized mainly on the ligands, and a t_{2g} below e_g splitting of the metal 3*d* orbitals. The crystal field splitting should be substantial, with t_{2g} (expected HOMO) below the unfilled e_g LUMO.

All the methods give this general orbital pattern. A striking difference here is that all the KS and HF levels are up (indeed at positive energy), while the EH levels are down in energy. This is a consequence of the large negative charge on the molecule. The extended Hückel method ignores electron repulsion; therefore, its energy levels are low in energy. An isolated CrH_6^{6-} is unrealistic; once the ion (even if it did exist) is surrounded by countercations, its levels will move down in energy.

If we compare the virtual orbital levels (cf. Figure 7), we see that the ordering of the calculated virtual KS energy levels is identical with that of HF orbitals but is significantly different from that of eH energies. This is illustrated dramatically by the LUMO—in the DF/HF calculations this orbital is not the expected e_g symmetry, but a t_{1u} orbital instead. We find the expected[52] "LUMO" (mainly $d_{x^2-y^2}$ and d_{z^2}, e_g) at much higher energy, above the t_{1u}, a_{1g} orbitals of type III, and another t_{1u}, a higher order type IV orbital (cf. Figure 6). This is a nice example—as mentioned at the beginning of the paper—of the fact that the borderline between type III and type IV orbitals is not sharp.

There is no doubt from these calculations that all chemically expected orbitals can be found in the various computational schemes (eH, KS, and HF). We can map all eH-like orbitals (which we want to assume as chemically meaningful; however, one can look at them also as an arbitrarily chosen reference system) to orbitals in the KS (and HF) picture. The KS and HF orbital energy positions relative to eH orbitals can be interchanged among themselves (e.g. the empty t_{1u} and a_{1g} orbitals (cf. Figure 7); or by virtual type IV orbitals).

2.6. A Second-Row Transition-Metal Complex, $PdCl_4^{2-}$. So far we have shown that KS orbitals are able to describe HF orbitals qualitatively and, after suitable scaling, also quantitatively (the HF and KS terms can be exchanged in this sentence). We finish this paper by discussing the calculated energy levels of a representative second-row transition-metal complex, the square-planar $PdCl_4^{2-}$. The KS eigenvalues of $PdCl_4^{2-}$ (plotted in Figure 8) show again, impressively, the compression and the $ax + b$ shift of the KS orbitals relative to HF orbitals. This systematic linear dependency can be nicely seen in Figure 9.

We calculated the scaling parameters as $a_{PdCl_4^{2-}}^{occ} = 0.27$, $b_{PdCl_4^{2-}} = 1.54$ eV, and $a_{PdCl_4^{2-}}^{virt} = 0.26$. The value of $a_{PdCl_4^{2-}}^{virt}$ differs significantly from that found for $a_{H_2O}^{virt}$ and $a_{N_2}^{virt}$, but the scaling parameter for the occupied orbitals,

(51) Cade, P. E.; Sales, K. D.; Wahl, A. C. *J. Chem. Phys.* **1966**, *44*, 1973.

(52) According to the simple crystal field considerations and eH calculations. We want to be a little careful here and refrain from saying which order is "correct".[53]

$a_{PdCl_4^{2-}occ} = -0.27$, is nicely close to -0.24 (H_2O) and -0.28 (N_2). It remains to be seen if there is meaning in this. What orbitals would one expect for $PdCl_4^{2-}$? Aside from core orbitals of Pd and Cl (including the $a_{1g} + b_{1g} + e_u$ Cl 2s set) we would expect lower lying Pd−Cl bonding orbitals of $a_1 + b_{1g} + e_u$ symmetry, and Cl lone pairs spanning $a_{1g} + b_{2g} + e_u + a_{2u} + b_{1g} + e_g + b_{2u} + e_u + a_{2g}$ representations. The Pd levels should follow—for these we expect a characteristic 4 below 1 splitting of a square-planar complex. The LUMO should be the $d_{x^2-y^2}$ orbital of b_{1g} symmetry.

For the palladium complex, the energy ordering of the Pd−Cl bonding orbitals a_1, e_u, and b_{1g} (the lowest occupied orbital block in Figure 8) is in excellent agreement for all the methods. Some occupied orbitals of higher energy (Cl lone pairs and Pd d orbitals) are interchanged in order (cf. Figure 8; for clarity, the symmetry of only the highest seven occupied orbitals is given). For instance the eH calculations lead to a HOMO of b_{2g} symmetry, while the HF and DF calculations have an a_{2g} HOMO. In contrast to the previously discussed CrH_6^{6-} complex, the virtual orbitals of type IV for the $PdCl_4^{2-}$ complex are nicely separated energetically from the virtual type III orbitals. With all method we find consistently a LUMO of b_{2g} symmetry. The trends previously obtained for the main-group-element molecules thus hold up for $PdCl_4^{2-}$.

3. Summary

Let us return to the title question: What meaning is there to the KS orbitals and eigenvalues? If we wish to use KS orbitals to rationalize chemical phenomena, we have to identify the order, symmetry, and shape of KS orbitals. When we are dealing with unoccupied orbitals, we have to distinguish in some cases between interchanged virtual orbitals of type III and type IV. Once this is done, then we think one may apply KS orbitals in a qualitative manner in MO arguments, in the way we are comfortable to doing with eH orbitals. Their number, symmetry properties, and shape are just like those of the expected one-electron orbitals. The situation is much like Baerends describes—these seem to be the orbitals a qualitative, chemical analysis needs.[13,14] Also, as a reviewer remarks, "since $\rho(r) = \sum_i |\varphi_{i,KS}|^2$, the shape and size of the KS orbitals is in case of a 'good' V_{KS} (KS potential) more 'physical' than those of other single-particle approximations".

If we want to go a step beyond a qualitative interpretation and look at orbital energies as rough ionization potentials, and if the DFT calculations are done with commonly used potentials, then it appears we must take the absolute constant and linear orbital energy shift into account by applying a suitable $ax + b$ scaling. Perhaps the situation will change with new functionals and new methods.[55]

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(53) Cf. the case of the lowest excitation (t_{2g} to e_g calculated with eH) in $Cr(CO)_6$ which was recently reassigned in: Pollak, C.; Rosa, A.; Baerends, E. J. *J. Am. Chem. Soc.* **1997**, *119*, 7324.

(54) Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 7132.

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