On Relativity, Bonding, and Valence Electron Distribution

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The scalar relativistic contributions to bond or atomization energies of homo- or hetero-polar s−p-bonded atoms, $\Delta^{\mathrm{rel}}E$(bond), correlate well with the changes on bond formation of the electron density, integrated throughout the spatial K-shell region of the heavy nucleus, $\Delta^{\mathrm{bond}}\rho_{\mathrm{K-region}}$, times Z^4, where Z is the nuclear charge. The "bond density changes" in the innermost atomic core regions, however, have no direct simple relationship to the electron density reorganizations in the outer atomic valence shell regions, which determine the nonrelativistic main contribution to the bond energy, $\Delta^{\mathrm{nonrel}}E$(bond). Also, scalar relativistic bond energy changes and bond length changes, $\Delta^{\mathrm{rel}}R_e$, are not directly correlated. Namely, $\Delta^{\mathrm{rel}}E$(bond) correlates with the difference $\Delta^{\mathrm{bond}}\rho_{\mathrm{K-region}}$, whereas $\Delta^{\mathrm{rel}}R_e$ correlates with the derivative $(\mathrm{d}\rho_{\mathrm{K-region}}/\mathrm{d}R)$. Reducing the internuclear distance from the separated to the united atom limit through the equilibrium distance value, R_e, the density around the nucleus at first decreases in many cases, goes through a minimum, and finally increases again. Therefore $(\mathrm{d}\rho_{\mathrm{K-region}}/\mathrm{d}R)$ may be positive or negative at R_e.

1. Introduction

Relativistic effects significantly change the valence properties of heavy element compounds. The same physical mechanisms operate in heavy and in light systems. The lighter systems are easier to understand, because first-order nondegenerate or near-degenerate perturbation theory (FOPT) is often sufficient and can be interpreted more easily. Electron correlation will be accounted for approximately at the level of density functional theory. It will also be cross-checked in a few cases by more sophisticated correlation methods.

Several years ago Wang[1] and Schwarz et al.,[2] and again more recently other researchers,[3−7] found that the scalar relativistic effects *reduce* the absolute value of the bond or atomization energies (atomization energy is the sum of two-atomic bond energies) of many light p-block molecules (i.e., *raise* the values of their bond energies, which are defined as negative). On the other hand, *positive* and *negative* relativistic contributions to bond energies were obtained for a more comprehensive set of molecules.[1,2,8,9]

The *scalar relativistic effects* comprise the direct mass−velocity and scalar spin-Darwin contributions, and the so-called indirect effects caused by the Coulomb repulsion between the *relativistically modified* orbitals. In addition, there are also the *vectorial spin-dependent* relativistic bond energy contributions, which are of orders of magnitude similar to the scalar ones.

A more detailed inspection of the published numerical data[1−7] on p-block elements suggests that the total scalar relativistic bond energy reduction can be approximated as a sum of diatomic relativistic bond energy increments. For bonds between H and a second- or third-row atom the increments range from 1 meV up to 10 meV. For bonds between two second-row atoms, the order of magnitude of the increments is about 10 meV; and for bonds from third-row atoms to third- or second-row ones, the increments are about 20 meV. The simple approach of Martin et al.[4] applying monatomic increments and formal bond orders reproduces the data only at a moderate accuracy.

To achieve further insight into the mechanisms of relativistic effects in chemical bonding, we have investigated the following light molecules, containing oxygen as the 'relativistic' atom: OH, H_2O, O_2, BeO, Li_2O, F_2O. The ground states of the respective atoms and molecules are $O(2p^4\ {}^3P_2)$, $H(1s\ {}^2S_{1/2})$, $Li(2s\ {}^2S_{1/2})$, $Be(2s^2\ {}^1S_0)$, $F(2p^5\ {}^2P_{3/2})$, $OH(\pi^3\ {}^2\Pi_{3/2})$, $H_2O({}^1A_1)$, $Li_2O({}^1\Sigma^+)$, $BeO({}^1\Sigma^+)$, $O_2({}^3\Sigma^-)$, $F_2O({}^1A_1)$. Concerning the structural parameters, see Table 1B. This set of molecules contains homopolar and heteropolar bonds, with oxygen being the negative or positive partner. In addition, a larger sample of heavier compounds from all blocks of the periodic table is also reinvestigated here.[1]

Spin−orbit (s−o) level splittings are qualitatively sketched in Figure 1 at the first-order level. Neglecting correlation effects, changes of the atomic orbitals (AO), and other higher order effects, one expects no significant s−o modification of the bond energy of OH and O_2, but bond destabilizations of about $^1/_2\cdot\lambda_{\mathrm{O2p}}$ for H_2O, Li_2O, and BeO, and of $^1/_2\cdot\lambda_{\mathrm{O2p}} + 1\cdot\lambda_{\mathrm{F2p}}$ for F_2O. (For general qualitative explanations of s−o-bond effects, see refs 8−11.) λ_{O2p} means the O-2p orbital s−o splitting parameter. The experimental atomic values of λ_{2p} for $O({}^3P)$ and for $F({}^2P)$ are 19 and 33 meV, respectively (derived from refs 12 and 13).

Concerning the *scalar relativistic effects,* we note that s valence AOs, in general, are relativistically stabilized, fractionally by the order of $(Z/c)^2$, see Appendix I and Table 3 below.[8,14] Here Z is the nuclear charge, and c the velocity of light in atomic units ($c = 1/\alpha = 137.036$). In oxygen, the 2s stabilization is about −40 meV. Concerning p valence AOs, the $p_{1/2}-p_{3/2}$ j-weighted averages $\bar{p}$ of most of the p-group atoms are weakly

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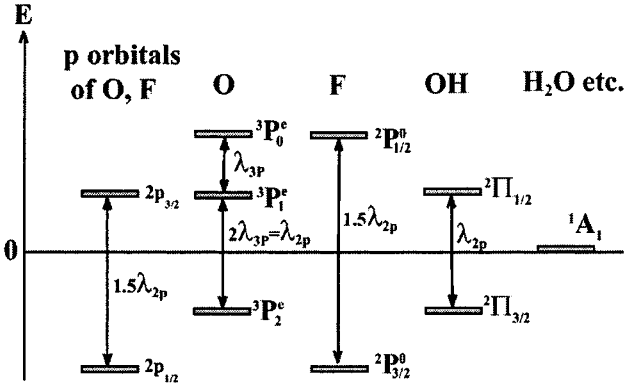

Figure 1. Sketch of spin−orbit splittings at the level of the first-order frozen orbital−*ls* coupling model. λ_{2p} is the 2p orbital spin−orbit parameter of the O atom (or F atom, respectively).

destabilized (except for the heaviest atoms in the lower right corner of the periodic table, see Table 3D). The fractional 2p destabilization in the second row of the periodic table (B to Ne) is comparatively "large" in units of $(Z/c)^2$, but its value is still only about +9 meV for O.[14]

Because the valence s AOs, and for most atoms also the $p_{1/2}$ AOs, are relativistically stabilized, one might at first expect that relativistic s−p-bond stabilization will occur for electronic charge transfer to the heavier atom. However, this turns out not to be the case in general. Then, one might expect, the more pronounced the s-to-p promotion and hybridization upon bond formation, the more relativistic bond destabilization. However, this expectation is also not fully corroborated by the calculations presented below.

The computational details of our investigation are described in Section 2. The calculated relativistic changes of bond energy and bond length are presented and discussed in relation to orbital populations and spatial electronic density distributions in Section 3. The final conclusions are given in Section 4. The relativistic atomic s and p orbital corrections are tabulated in Appendix I, and a comment on local properties in relativistic quantum chemistry is made in Appendix II.

2. Calculations

The light and heavy atoms and molecules mentioned in the Introduction were calculated and analyzed at the density functional level. We have applied the Amsterdam Density Functional (ADF) package.[15] Both the all-electron and the frozen-core orbital options were used. The LDA and Becke−Vosko−Perdew[16] combination of density functionals (DF) (BVP) was used. Extended Slater basis sets of the uncontracted valence triple−polarization double-ζ type (3s3p2d2f)[17] were applied.

In addition, a few light systems were investigated at the ab initio MRCISD(q) and CCSD(T) levels (multireference configuration interaction with single and double substitutions and Davidson's correction; coupled cluster with singles, doubles, and perturbative triples). The MOLPRO package[20] was used. The extended cc-pCVQZ Gaussian basis sets of Dunning[26] were applied (fully uncontracted, but without g functions in the s−o calculations).

Concerning the relativistic corrections, first-order Hamiltonians were applied. In the DF case, we used a Breit−Pauli-type Hamiltonian, transformed so[20] that it resembles the numerically stable relativistic Dirac Perturbation Theory (DPT)[21,22] at first order. In the ab initio case, the first-order scalar relativistic corrections were determined with DPT at the correlated CCSD(T) level.[25] The first-order s−o level splittings were calculated by means of the Breit−Pauli s−o operator at the MRCISD(q) level. Note that the Breit−Pauli s−o operator is exactly the same as the s−o part of the first-order DPT operator.[22]

The energy and electron density contributions from specified regions of space were determined individually with the help of Boerrigter's integration scheme.[19] Thereby, the total relativistic change of the bond energy of a molecule can be, within the framework of first-order perturbation theory, partitioned rather uniquely into contributions from the individual atoms. Theoretical subtleties of such a partitioning at the FOPT level have been discussed in detail elsewhere.[8]

3. Results and Discussion

3.1. Relativistic Bond Energy and Valence Shell Populations. The calculated relativistic energy corrections are presented in Table 1. Positive values indicate relativistic destabilization of the molecules. The s−o contributions are of the expected[10,11] sign and order of magnitude (compare Figure 1).

The present scalar relativistic corrections of the molecular atomization energies, $\Delta^{\text{scal.rel}}E$(bond), lie within the scatter of results of other authors (cf. Table 1B). The present first-order DPT-CCSD(T) results from extended basis sets are expected to be the most accurate estimates of $\Delta^{\text{rel}}E$ for the systems studied here.

$\Delta^{\text{rel}}E$(bond) does not correlate well with the total effective atomic charges on the oxygen. Concerning the Mulliken charges (Figure 2A), a low-quality linear correlation seems to exist (correlation coefficient $k = 0.76$), but the respective line (not shown in Figure 2A) would largely deviate from the reference origin of the oxygen atom at ΔE(bond) = 0, $Q_{\text{eff}} = 0$. (We do not consider here the principal problem of Mulliken's definition of charges and orbital populations, which yields nonunique values.)

Physically better defined parameters such as the Wigner−Seitz or Voronoi charges also do not satisfactorily correlate with $\Delta^{\text{scal.rel}}E$(bond); see Figure 2B (the correlation is even worse, $k = 0.71$). And the correlation with the oxygen 2s-AO population (Figure 3) is not better. The situation is not improved very much for other choices of parameters. We had already found in an investigation of more than 30 diverse s−p−σ-bonded heavy molecules[1,2] that no simple relation exists between the scalar relativistic bond energy contributions and the electronic distributions in the valence shells of the bonded atoms.

3.2. Relativistic Bond Energy and the Spatial Neighborhood of the Nuclei. In Appendix II we argue that, despite Heisenberg's uncertainty principle, some basis still exists to talk about local energy contributions from specific regions of space, such as momentum-dependent local kinetic energies. Namely, valence electrons behave relativistically when they dive into an atomic core and become 'relativistically fast' near a nucleus.[27] That is, the direct relativistic contributions to the valence energy physically emerge from the neighborhood of the nuclei.[28,29] (Sometimes it is reported that the relativistic change of energy of an atomic valence orbital is caused by orthogonality of the valence orbitals on the relativistically modified inner core orbitals of the same atom. This is not true; see ref 29.) Accordingly, we expect the scalar relativistic atomization energy contribution, $\Delta^{\text{scal.rel}}E$(bond), to be a sum of increments from the different regions of each bonded atom in the molecule. The largest relativistic bond increments should be directly proportional to the change of density (upon bond formation) in the neighborhood of the heavy nuclei.

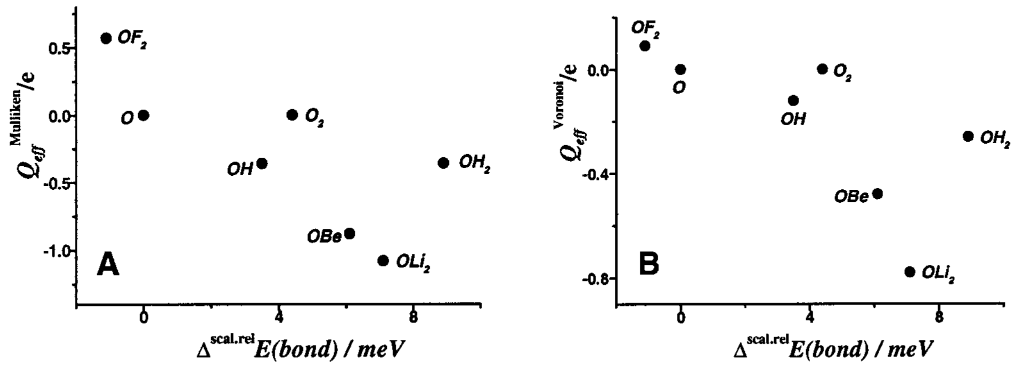

Figure 2. Calculated scalar relativistic atomization energy contributions, $\Delta^{scal.rel}E$(bond), versus effective charge on the oxygen atom, from ADF calculations. (A) $Q_{eff}^{Mulliken}$; (B) $Q_{eff}^{Voronoi}$.

TABLE 1: Relativistic Atomization Energy Contributions (in meV = 23 cal/mol ≈ 0.1 kJ/mol; negative means stabilization)

A. experimental and calculated spin−orbit stabilizations

system	state	s−o stabilization exp.[13,40]	calc. MRCISD(q) & FODPT	calc. DF−BVP & Pauli
O	$^3P_2{}^e$	−9.5	−9.6	−11.8
F	$^2P_{3/2}{}^o$	−16.7	−16.1	−20.6
OH	$^2\Pi_{3/2}$	−7.8	−8.6	−11 0.0

B. calculated scalar relativistic energy contributions from the O atom for the molecular valence shell,
and total relativistic bond energy change of the molecules

		scalar relativistic valence shell energy			total relativistic change energy of atomization energy	
system[a]	state	calc. CCSD(T) & FODPT	calc. DF−BVP & Pauli	other authors[3−7]	calc. CCSD(T) & FODPT	calc. DF−BVP & Pauli
OH(97)	$^2\Pi_{3/2}$	+5.0[b]	+3.6	4.3, 4.8, 5.2, 6.2	+6.2	+4.3
OH_2 (96;104)	$^1A_1$	+11.0[b]	+8.9	11.3, 13.0, 13.3, 14.0	+20.9	+20.7
OLi_2 (165)	$^1\Sigma^+{}_{g,0+}$		+7.1			+18.9
OBe (133)	$^1\Sigma^+{}_{0+}$		+6.6	4.7, 5.4		+17.9
O_2 (120.8)	$^3\Sigma^-{}_{g,0+}$		+4.4[c]	2.2, 2.7, 3.2, 6.9		+28.0
OF_2 (142;105)	$^1A_1$		−1.1[c] +12.9[c]			+77.7

[a] In parentheses: bond length (in pm); and where applying bond angle (in degree). [b]Reference value is 1515.4 meV (1499 meV by ref 41); i.e., valence shell only; [c]per each O and F atom, i.e., $\Delta E(O_2) = 2\cdot\Delta E(O)$ and $\Delta E(OF_2) = \Delta E(O) + 2\cdot\Delta E(F)$.

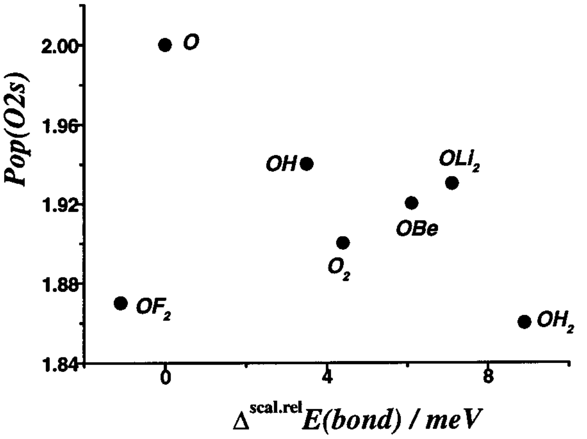

Figure 3. Calculated scalar relativistic atomization energy contributions, $\Delta^{scal.rel}E$(bond), versus O-2s AO population, Pop(O2s), from ADF calculations.

Therefore, we have determined the change caused by bond formation, Δ^{bond}, of the electronic density within the region of the K shell, $\langle\rho\rangle_{K-region}$. The outer radius of a K shell is here defined by the inner nodes of the respective atomic outer s orbitals. According to this definition, the respective $\langle...\rangle_{K-region}$ integral values are not very sensitive to small changes of the K-shell radii values, because the radial density of the s orbitals has a minimum there.

TABLE 2: The Orbital Populations, the Atomic Mulliken- ($Q_{eff}^{Mulliken}$) and Voronoi- Deformation Charges ($Q_{eff}^{Voronoi}$) in e, the Change of Density in the K-shell of Oxygen[b] Due to Bond Formation ($\Delta^{bond}\langle\rho\rangle_{O-K-region}$), in 10^{-3} e, and Relativistic Change of Bond Length ($\Delta^{scal.rel}R_e$) in pm

system	O 2s	O 2p	O d,f	$Q^{Mulliken}$	$Q^{Voronoi}$	$\Delta^{bond}\langle\rho\rangle_{O-K}$[a]	$\Delta^{scal.rel}R_e$
OH_2	1.86	4.46	0.05	−0.36	−0.26	−2.83	> +0.01
OH	1.94	4.39	0.03	−0.36	−0.12	−1.23	> +0.01
OLi_2	1.93	5.15	0.01	−1.08	−0.78	−1.84	−0.015
OBe	1.92	4.91	0.03	−0.88	−0.48	−1.65	> +0.01
O_2	1.90	4.03	0.07	0.0	0.0	−1.18	+0.025
O	2	4	0	0	0	0	
OF_2	1.87	3.53	0.00	+0.57 −0.28[b]	+0.09 −0.05[b]	+0.08 −2.88[b]	−0.47

[a] Reference value is 2000 me. Negative sign means reduced electron density around the oxygen nucleus in the molecule. [b] Values on each F atom in the OF_2.

The $\Delta^{bond}\langle\rho\rangle_{K-region}$ values of oxygen are given in Table 2. They are plotted in Figure 4 versus the $\Delta^{scal.rel}E$(bond) values from Table 1B. A reasonable linear relationship exists with *k* = 0.98. Figure 4 also indicates that accurate data make the linearity even better.

It is remarkable that both the all-electron optimized core orbital and the frozen core orbital results lie on the same correlation line. In the frozen-core representation, both the bond energy and the bond density contributions (also those in the

TABLE 3: Fractional Relativistic Correction Factors γ (eq A0) of Energies ϵ (upper entries) and Radii $\langle r\rangle$ (lower entries) of the Atomic Valence s and p Dirac−Fock Orbitals[14]

A. s

${}_{1}$H	0.25													${}_{2}$He	0.2
	0.33														0.24
${}_{3}$Li	0.17	${}_{4}$Be	0.20	${}_{5}$B	0.32	${}_{6}$C	0.10	${}_{7}$N	0.11	${}_{8}$O	0.48	${}_{9}$F	0.51	${}_{10}$Ne	0.53
	0.19		0.21		0.26		0.29		0.31		0.32		0.33		0.33
${}_{11}$Na	0.200	${}_{12}$Mg	0.429	${}_{13}$Al	0.291	${}_{14}$Si	0.335	${}_{15}$P	0.364	${}_{16}$S	0.385	${}_{17}$Cl	0.402	${}_{18}$Ar	0.416
	0.204		0.322		0.220		0.230		0.235		0.240		0.243		0.246
${}_{19}$K	0.195	${}_{20}$Ca	0.187	${}_{31}$Ga	0.436	${}_{32}$Ge	0.455	${}_{33}$As	0.427	${}_{34}$Se	0.426	${}_{35}$Br	0.425	${}_{36}$Kr	0.425
	0.196		0.183		0.323		0.301		0.283		0.273		0.265		0.259
${}_{37}$Rb	0.213	${}_{38}$Sr	0.347	${}_{49}$In	0.471	${}_{50}$Sn	0.454	${}_{51}$Sb	0.442	${}_{52}$Te	0.432	${}_{53}$I	0.425	${}_{54}$Xe	0.419
	0.215		0.238		0.343		0.313		0.293		0.278		0.267		0.258
${}_{55}$Cs	0.096	${}_{56}$Ba	0.207	${}_{81}$Tl	0.561	${}_{82}$Pb	0.531	${}_{83}$Bi	0.509	${}_{84}$Po	0.492	${}_{85}$At	0.479	${}_{86}$Rn	0.468
	0.094		0.204		0.430		0.388		0.360		0.340		0.324		0.312

B. $p_{1/2}$

${}_{5}$B	−0.11	${}_{6}$C	0.04	${}_{7}$N	0.17	${}_{8}$O	0.30	${}_{9}$F	0.42	${}_{10}$Ne	0.53
	0.05		0.15		0.22		0.28		0.33		0.37
${}_{13}$Al	−0.004	${}_{14}$Si	0.119	${}_{15}$P	0.214	${}_{16}$S	0.294	${}_{17}$Cl	0.363	${}_{18}$Ar	0.425
	0.082		0.15		0.22		0.28		0.33		0.37
${}_{31}$Ga	0.097	${}_{32}$Ge	0.217	${}_{33}$As	0.300	${}_{34}$Se	0.365	${}_{35}$Br	0.418	${}_{36}$Kr	0.464
	0.190		0.232		0.252		0.264		0.273		0.279
${}_{49}$In	0.156	${}_{50}$Sn	0.261	${}_{51}$Sb	0.331	${}_{52}$Te	0.384	${}_{53}$I	0.426	${}_{54}$Xe	0.461
	0.233		0.259		0.269		0.274		0.277		0.278
${}_{81}$Tl	0.257	${}_{82}$Pb	0.358	${}_{83}$Bi	0.421	${}_{84}$Po	0.466	${}_{85}$At	0.501	${}_{86}$Rn	0.528
	0.333		0.348		0.349		0.347		0.345		0.342

C. $p_{3/2}$

${}_{5}$B	−0.33	${}_{6}$C	−0.33	${}_{7}$N	−0.35	${}_{8}$O	−0.39	${}_{9}$F	−0.43	${}_{10}$Ne	−0.47
	−0.15		−0.13		−0.13		−0.13		−0.14		−0.15
${}_{13}$Al	−0.290	${}_{14}$Si	−0.277	${}_{15}$P	−0.281	${}_{16}$S	−0.290	${}_{17}$Cl	−0.302	${}_{18}$Ar	−0.315
	−0.143		−0.116		−0.102		−0.094		−0.088		−0.084
${}_{31}$Ga	−0.244	${}_{32}$Ge	−0.236	${}_{33}$As	−0.244	${}_{34}$Se	−0.255	${}_{35}$Br	−0.266	${}_{36}$Kr	−0.277
	−0.080		−0.063		−0.057		−0.055		−0.053		−0.052
${}_{49}$In	−0.232	${}_{50}$Sn	−0.224	${}_{51}$Sb	−0.230	${}_{52}$Te	−0.239	${}_{53}$I	−0.247	${}_{54}$Xe	−0.256
	−0.059		−0.046		−0.041		−0.039		−0.038		−0.037
${}_{81}$Tl	−0.257	${}_{82}$Pb	−0.253	${}_{83}$Bi	−0.261	${}_{84}$Po	−0.271	${}_{85}$At	−0.281	${}_{86}$Rn	−0.291
	−0.061		−0.047		−0.042		−0.040		−0.039		−0.038

D. $\bar{p}$

${}_{5}$B	−0.26	${}_{6}$C	−0.21	${}_{7}$N	−0.18	${}_{8}$O	−0.16	${}_{9}$F	−0.15	${}_{10}$Ne	−0.14
	−0.08		−0.04		−0.01		0.00		0.02		0.02
${}_{13}$Al	−0.194	${}_{14}$Si	−0.145	${}_{15}$P	−0.115	${}_{16}$S	−0.095	${}_{17}$Cl	−0.079	${}_{18}$Ar	−0.066
	−0.068		−0.029		−0.006		0.009		0.020		0.029
${}_{31}$Ga	−0.129	${}_{32}$Ge	−0.082	${}_{33}$As	−0.059	${}_{34}$Se	−0.043	${}_{35}$Br	−0.031	${}_{36}$Kr	−0.022
	0.009		0.034		0.045		0.050		0.054		0.057
${}_{49}$In	−0.099	${}_{50}$Sn	−0.055	${}_{51}$Sb	−0.033	${}_{52}$Te	−0.018	${}_{53}$I	−0.007	${}_{54}$Xe	0.001
	0.036		0.053		0.059		0.062		0.064		0.065
${}_{81}$Tl	−0.065	${}_{82}$Pb	−0.018	${}_{83}$Bi	0.007	${}_{84}$Po	0.024	${}_{85}$At	0.037	${}_{86}$Rn	0.047
	0.059		0.073		0.077		0.077		0.077		0.077

spatial core regions near the nuclei) are completely caused by the valence electrons, i.e., the outer and inner wiggles of the valence orbitals. Even the Hellmann-Feynman forces,[30] which are extremely sensitive to tiny details of the total electronic density near the nuclei, can be well reproduced in the frozen-core orbital approximation. One should also remember that any partitioning into core and valence orbital contributions is somewhat arbitrary, whereas the total expectation values, such as $\mathbf{\Delta}^{\mathrm{scal.rel}}E(\mathrm{bond})$ or $\Delta^{\mathrm{bond}}\langle\rho\rangle_{\mathrm{K-region}}$, are unique.

The relativistic energy contributions of hydrogen-like atomic orbitals vary with the nuclear charge as Z^4. Indeed $\Delta^{\mathrm{scal.rel}}E(\mathrm{bond})$ correlates well with $\Delta^{\mathrm{bond}}\langle\rho\rangle_{\mathrm{K-region}}\cdot Z^4$ for a large set of s−p−σ-bonded molecules with a single heavy atom (Figure 5, see also refs 1 and 2), where $k = 0.95$:

$$\Delta^{\mathrm{scal.rel}}E(\mathrm{bond}) \approx -21\ \mathrm{V}\cdot\Delta^{\mathrm{bond}}\langle\rho\rangle_{\mathrm{K-region}}\cdot Z^4/c^2 \qquad (1)$$

The respective slope of −21 V for heavy atomic molecules agrees well with the one from Figure 4 for oxygen compounds, which is −22.5 V (i.e., $-103\ \mathrm{V}\cdot Z^4/c^2$, where Z/c is 8/137 for oxygen). Most molecules with a heavy s-block element in Figure 5 show relativistic bond energy increases, whereas most molecules with a heavy p−d−f-block element show relativistic bond energy decreases, as do the oxygen systems. Both correlation lines in Figures 4 and 5 nicely pass close to the origin.

After this work had been finished, Kedziora et al.[6] published extensive investigations on 222 molecules of the so-called 'G3/99 formation set'. These authors found a very good correlation between the total scalar relativistic energy contributions of the molecules, $\Delta^{\mathrm{scal.rel}}E(\mathrm{total})$, and the sum of the electron densities at the nuclei, ρ_n ($r = 0$), times the respective Z values:

$$\Delta^{\mathrm{scal.rel}}E(\mathrm{total}) \approx -2.035\ \mathrm{V}\ \text{Å}^3\cdot\Sigma_{\mathrm{nuclei}}\ \rho_n(r = 0)\cdot Z_n/c^2 \qquad (2)$$

Because the radii of the K-shells are about 1 Å/Z, we get $\langle\rho\rangle_{\mathrm{K-region}} \sim \rho(r = 0)\cdot\text{Å}^3/Z^3$. So, eqs 1 and 2 correspond to each other, at least concerning the functional dependencies. However, $\Delta^{\mathrm{scal.rel}}E(\mathrm{bond})$ seems to correlate only qualitatively with $Z\cdot\Delta^{\mathrm{bond}}\rho(r = 0)$.[6] $\Delta^{\mathrm{rel}}E(\mathrm{bond})$ is only a very small, sensitive fraction of $\Delta^{\mathrm{rel}}E(\mathrm{total})$, and $\Delta^{\mathrm{bond}}\rho(r{=}0)$ is also a sensitive property at a single point. In contrast, $\Delta^{\mathrm{bond}}\langle\rho\rangle_{\mathrm{K-region}}$ is an integral property, which also accounts for inner density polarizations and some p-AO density. Therefore, a better correlation of $\Delta^{\mathrm{scal.rel}}E(\mathrm{bond})$ with $\Delta^{\mathrm{bond}}\langle\rho\rangle_{\mathrm{K-region}}\cdot Z^4$ (eq 1) than with $\rho(r = 0)\cdot Z$ (corresponding to eq 2) seems reasonable.

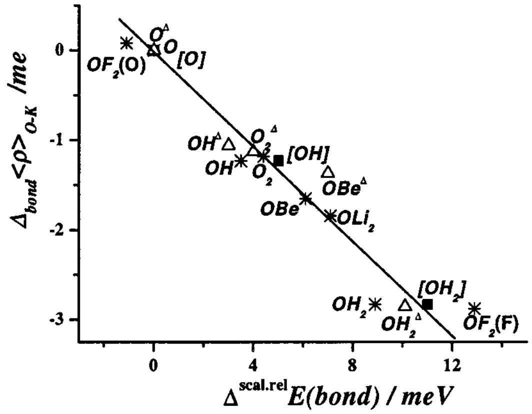

Figure 4. Calculated scalar relativistic atomization energy contributions, $\Delta^{scal.rel}E$(bond) in 10^{-3} eV. ■, accurate CCSD(T)−FODPT approach, molecular formula in square brackets; △, DF (ADF−BVP−Pauli) approach, molecular formula with superscript Δ; *, DF estimate by frozen-core orbital approximation. Plotted versus change of electronic charge in the K-shell region of the oxygen atom due to bonding, $\Delta^{bond}\langle\rho\rangle_{O-K-region}$, in 10^{-3} e (from DF calculations). In OF_2, there is a small contribution to $\Delta^{scal.rel}E$(bond) from oxygen [OF_2(O)] and bigger ones from the fluorines [OF_2(F)]. The latter contributions to ΔE(bond) are also plotted, versus $\Delta^{bond}\langle\rho\rangle_{F-K-region}$ of the F−K shell, times $(9/8)^4$ where (9/8) is the ratio of nuclear charges of F and O.

Concerning the relation between relativistic energy and $Z^4 \bullet \langle\rho\rangle_{K-region}$, we add the following remarks. Depending on the type of representation, the first-order one-electron scalar relativistic operator is

$$-1/2mc^2 *\{p(E-V)p/2m\} \quad \text{(from direct Dirac perturbation theory),}$$

or

$$-1/2mc^2 *\{T^2 + [TV]\} \quad \text{(from Pauli perturbation theory),} \qquad (3)$$

or

$$-1/2mc^2 *\{(E-V)^2 - [pV]\cdot p/2m\}, \text{ etc.,}$$

where $T = p\cdot p/2m$ is the nonrelativistic kinetic energy corresponding to $T = (E-V)$, and where $[TV] = -\Delta V/2$ yields the Darwin term for Coulomb potentials. Although the density of the inner wiggles of the valence orbitals is small, both the nonrelativistic kinetic and potential energy contributions from any of the wiggles are all similarly large, $T \approx -V \gg -\epsilon$.[28] But they cancel each other nearly completely in the inner regions. The respective contributions of the relativistic expressions (3) become even more huge for the inner wiggles of the valence orbitals and no longer cancel each other. Each of the different representations (3) yields the largest contributions very near to the nuclei.[28]

3.3. Electron Difference Density Distributions due to Bonding. The electron "deformation" density distributions (DD) are conventionally defined as the difference between the molecular density and the superposed, spherically averaged densities of the ground configurations of the neutral atoms.[31] The DDs of BeO, OH, O_2, and OF_2 are plotted along the molecular axes in Figure 6.

Corresponding to the chemical formula of $Be^{\delta+}O^{\delta-}$, the molecular electron density in the beryllium region has decreased (Figure 6A), whereas in the valence shell around the oxygen K shell it has increased. However, in the oxygen core region the density nevertheless has decreased.

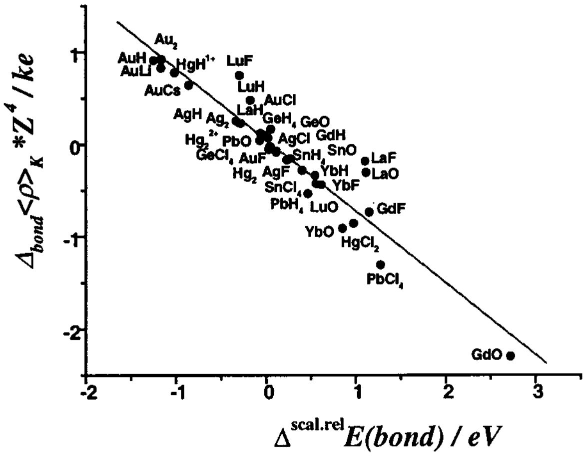

Figure 5. Calculated (ADF) scalar relativistic bond energy contributions, $\Delta^{scal.rel}E$(bond), in electronvolts, versus change of electronic charge in the K shell of the heavy atom, $\Delta^{bond}\langle\rho\rangle_K$, times its Z^4, in 10^3 e, for 30 molecules with a heavy atom from the s, the p, and the d−f blocks of the periodic system.

Concerning $O^{\delta-}H^{\delta+}$, we remember[32] that any bonded hydrogen has an increased electron density at the nucleus and on the bond axis. "Positively charged" bonded hydrogens are characterized by reduced electron density in a large region "behind" the proton (Figure 6B). Again the bonded $O^{\delta-}$ exhibits some electron density increase in the valence region, but density decrease at the nucleus.

In O_2 the neutral oxygen atoms, of course, do not show an average electron density increase in the valence region, but there still is an average density decrease in the K-shell region (Figure 6C). In all three cases of BeO, OH, and O_2, we note the pronounced charge asymmetry in the oxygen K shell, which yields a significant contribution to the binding Hellmann−Feynman forces.[30]

In $O^{\delta+}F^{\delta-}$ (Figure 6D) there is an average decrease of density in the oxygen valence shell, a pronounced charge asymmetry in the O−K shell, but very small change of total charge in the O−K shell. Not visible along the molecular axis in Figure 6D, there is, however, significant density reduction in the K-shells of the fluorine atoms before and behind the axis.

3.4. Bond Length and Bond Energy. According to chemical rules of thumb, inverse correlations exist between bond lengths and bond strengths, concerning, for instance, (more or less polar) covalent bonds,[33] hydrogen bonds,[34] etc. One might anticipate, therefore, that the relativistic reduction of the value of the bond energy of most p-block compounds, $|\Delta^{scal.rel}E(\text{bond})| < 0$, would go together with relativistic bond-length expansion, $\Delta^{scal.rel}R_e > 0$. On the other hand, it had been argued that, because of overlap and orbital orthogonality between the valence AOs of one atom and the core of the other bonded (heavy) atom, scalar relativistic effects should in general contract the bond lengths.[35]

In an analysis of the relativistic virial theorem, the following points had been noted.[36] First, at large internuclear distances (separated atom limit), the interaction energy is dominated by multipole, induction, and dispersion effects. In many cases relativistic orbital contraction dominates, and the electric moments, the polarizability, and the van der Waals constants are relativistically reduced. Then the value of the long-range interatomic attraction becomes reduced because of relativity. Second, at short distances (united atom limit), relativity stabilizes the compound system, because $\Delta^{rel}E \sim Z^4$. That is, $\Delta^{rel}E$ often increases at first for decreasing R, and then it decreases for small R values. An example of this rather common behavior is shown

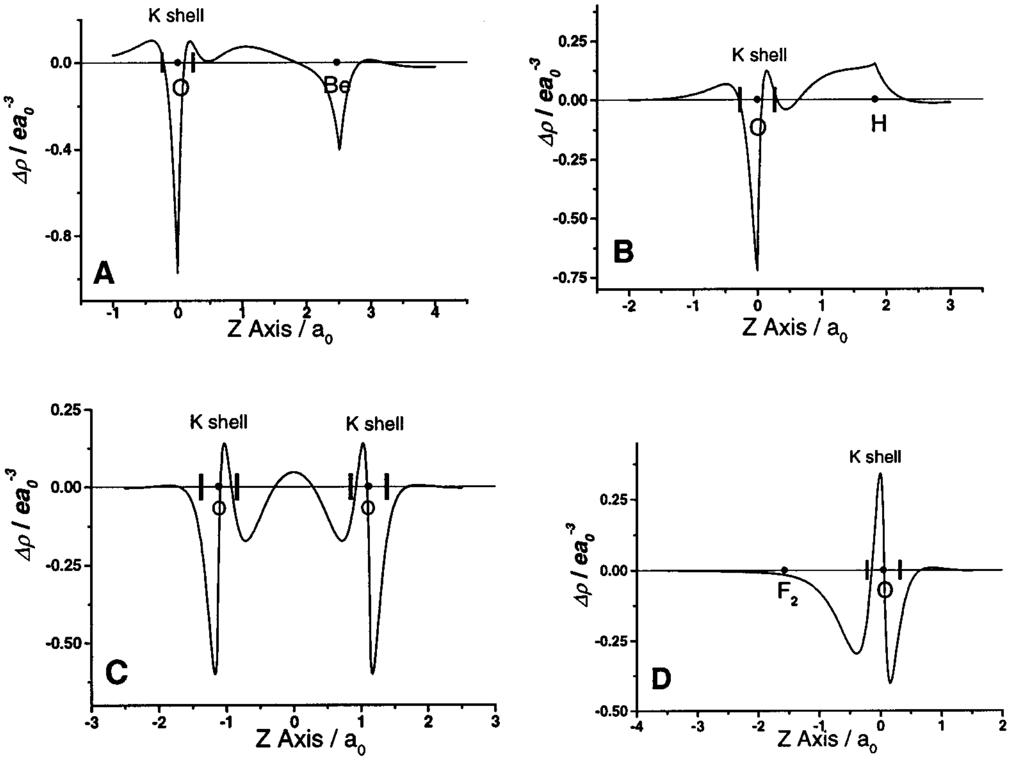

Figure 6. Difference of electronic density between superimposed spherical atoms and the bonded molecule, along the molecular axis. Negative means reduced density in the molecule. The nuclei are at ●, the extensions of the K shells are indicated by |. (A) BeO; (B) OH; (C) O_2; (D) OF_2 (the diagonal axis goes through the middle between the two F atoms, F_2).

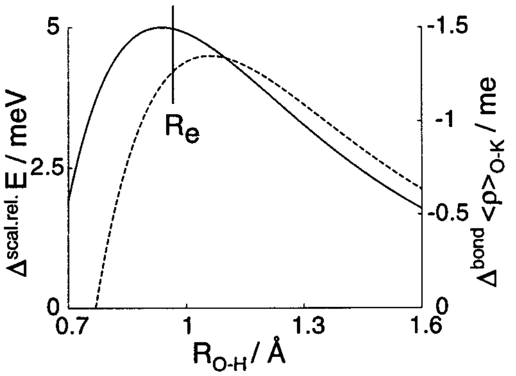

Figure 7. Scalar relativistic bond energy change, $\Delta^{scal.rel}E$(bond), left scale in 10^{-3} eV, and change of the electronic charge within the region of the K shell caused by bond formation, $\Delta^{bond}\langle\rho\rangle_{K-region}$, right scale in 10^{-3} e, for OH, versus the internuclear distance R in angstroms.

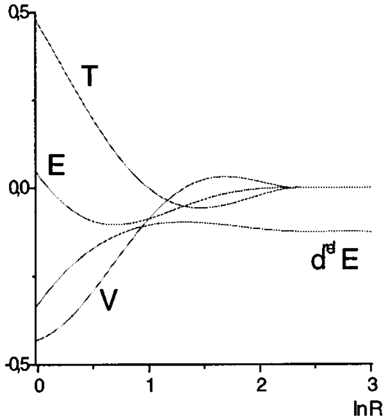

Figure 8. Kinetic energy T, potential energy V, total energy E, and relativistic contribution $\Delta^{rel}E$ to the total energy times c^2, $d^{rel}E = \Delta^{rel}E\cdot c^2$, versus logarithm of internuclear distance, ln R, of H_2^+, all quantities in atomic units.[36]

in Figure 7, where the bonding is mainly caused by oxygen-2p. Similar curves were obtained, for instance, for the pσ-bonded halogen dimers, for the thallium halides,[24b] and for the s-bonded H_2^+ (see Figure 8).[36]

The lighter p-block compounds evidently lie near the maximum of the $\Delta^{rel}E(R)$ curve, where the slope is very small. According to double-perturbation theory, the relativistic first-order change of bond length R_e is given by[37]

$$\Delta^{rel}R_e = -E^{11}/k = -(\partial^2 E/\partial \ln \alpha^2\, \partial R)_{Re}/(\partial^2 E/\partial R^2)_{Re} \quad (4)$$

where k is the force constant and α is the fine structure constant. Because E^{11}, i.e., the slope of the $\Delta^{rel}E(R)$ curve, is so small, $\Delta^{rel}R_e$ is comparatively small, too (see Table 2). For comparatively shorter R_e values, the slope is larger and positive, and one obtains larger bond contractions for both $\Delta^{scal.rel}E$(bond) > 0 (relativistic destabilization as for many p-block compounds), and for $\Delta^{scal.rel}E$(bond) < 0 (relativistic stabilization as for many s-block compounds).

4. Concluding Remarks

It is remarkable that the electron density near the nucleus can increase or decrease, in a given bond formation process, for both density increase and density decrease in the valence shell of the respective atom. This is so because several opposing tendencies contribute.

First, electric polarization and dispersion as well as orbital overlap effects at large internuclear distances in general transfer charge from the vicinity of the nuclei into the adjacent regions of the outer valence shells, thereby reducing the density around the nuclei. This raises the potential energy of the system. And the respective electron density delocalization results in a (somewhat larger) decrease of the kinetic energy, particularly of its bond-parallel component.[38,39] According to the negative signs in eq 3, relativity attenuates the nonrelativistic energy decrease.

Second, when overlap increases upon reducing the internuclear distance further, the Pauli principle (e.g., orthogonality of overlapping occupied orbitals in the standard independent electron model) keeps the valence density of one atom out of the core electrons' region of the other atom. But it increases the density at the nucleus because of the orthogonalization tails of the orbitals.[35] This holds for any type of valence overlap, i.e., also for p and d AOs, which have no (nonrelativistic) electron density contributions at the nuclei in the unperturbed atoms. The kinetic energy begins to increase because of the orthogonalization wiggles, and the potential energy begins to decrease. Because the kinetic term dominates in the relativistic corrections, eq 3, the change of trend upon shortening the internuclear distance occurs already at larger distances for the relativistic bond energy contribution $\Delta^{\mathrm{rel}}E(\mathrm{bond})$ than for the nonrelativistic one, $E(\mathrm{bond})$ (e.g., see Figure 8).

Third, at even shorter internuclear distances around the equilibrium separation R_e, valence orbital contraction toward the electronic potential wells is required to occur according to the virial theorem,[38,39] resulting in a density increase around the nucleus. This concerns particularly bonding s valence orbitals, while bonding pó orbitals contract less, and the pπ AOs undergo only little change.[42,43] Antibonding AO interaction causes an opposite orbital-expansion.

Fourth, as mentioned in the beginning, if bonding induces s−p promotional hybridization, i.e., angular deformation of the bonded atoms in the molecule, and reduces the s valence population (compare the AO population values in Table 2), the inner tail density of the s valence orbital at the nucleus should also decrease, although the total density in the valence shell does not change. (However, upon relativistic 'antiparallel' spin−orbit coupling, a relativistic $\mathrm{p}_{1/2}$ spinor obtains density at the nucleus.)

Finally, an increase of density on an atom increases the interelectronic repulsion, which expands the charge distribution in the valence shell. This is particularly pronounced for negatively charged atoms. Indeed, in second-row atoms, the density increase in the K-shell region is only in the percent range for a 100% increase of the 2s population (i.e., by one additional valence electron). So, only low-quality correlations were found between $\Delta^{\mathrm{scal.rel}}E(\mathrm{bond})$ and orbital populations or atomic charges in the valence shell.

As a result of these different mechanisms, sσ-bonded molecules adopt their equilibrium distance R_e, where the K-shell density is already increasing for decreasing distance, so $\Delta^{\mathrm{rel}}R_\mathrm{e} < 0$ and $\Delta^{\mathrm{rel}}E(\mathrm{bond})$ either $>$ or $<$ 0, whereas pσ-bonded molecules have their equilibrium distance not far from where the K-shell density is minimal, so $\Delta^{\mathrm{rel}}R_\mathrm{e} \approx 0$ and $\Delta^{\mathrm{rel}}E(\mathrm{bond}) > 0$.

Simple arguments in the literature such as "Electrons participating in bonding are drawn away from the nucleus to the bond center. Therefore bonding reduces the relativistic energy stabilization.", or those ones mentioned at the end of the section 1, must be applied with caution. Also the relations between $\Delta^{\mathrm{rel}}E(\mathrm{bond})$ and $\Delta^{rel}R_\mathrm{e}$ cannot be explained with the help of such naive inferences.

Generally speaking, the first-order differential relativistic effects are determined by the deformed (i.e., molecular) one- and two-particle density matrixes in conjunction with first-order relativistic integrals. For the systems studied here, the two-electron relativistic effects are small. Near the nuclei, the K-shell density dominates in the one-particle density matrix; therefore, a 'good' correlation is expected between (first order) relativistic effects and the K-shell density. However, for valence shells, generally the off-diagonal elements of the one-electron density matrix in an atom centered basis are not small, and therefore a good correlation between valence-shell density and relativity cannot be expected in general.

Quantum theory is a 'holistic' theory: Whole space and whole environment matters. However, because the wave function is analytic, already a small piece in some spatial domain determines the whole wave function. So in principle, any region of space can be used to explain the whole bonding mechanism. Furthermore, performing integral transformations and mathematical conversions, different weights can be attached to different spatial domains. A typical example is the transition probability between two extended Rydberg states: In the length formula, the dominant outer diffuse density of the states matters, while in the velocity and in particular in the acceleration formula the tiny inner orbital tails matter.

Using common formulations, the nonrelativistic s−p valence energy (concerning valence forces see below) comes dominantly from the outer atomic spatial shells, whereas the direct relativistic valence effects originate in these formulations dominantly from the innermost atomic core regions. The indirect relativistic effects come from the whole atomic region; they modify the orbital properties in first order of c^{-2}, but total energies and, accordingly, atomization energies, are influenced only in second order. This explains why also the heavy-atomic compounds with large indirect orbital reorganizations lie near the correlation lines of Figures 4 and 5. Scalar relativistic bond effects can be attributed dominantly to the contributions from the first half wave of atomic s orbitals (compare also refs 1, 2, and 28).

If very similar compounds are compared, such as different covalently bonded carbon atoms in organic chemistry, a linear relation may exist between the wave function at the nucleus and in the outer valence shell, e.g., between the chemical shift and the outer valence s population. However, this core-valence relation does not hold in general, as concerning the examples discussed above. We also note that the nonrelativistic valence effects are "determined" by the wave function in all spatial regions of the molecule, *if* the bonding *forces* are determined by integrating the Hellmann−Feynman[38] formula, where especially high weights are put on the regions near the nuclei.[30]

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Appendix I

Fractional Relativistic Correction Coefficients for Valence s and p AOs. The fractional relativistic correction of the energies ϵ and of the radii $\langle r\rangle$ of the atomic valence s and p Dirac−Fock orbitals[14] are represented in the form of "fractional relativistic correction factors" γ:

$$\Delta^{\mathrm{rel}}\epsilon/\epsilon = \gamma_\epsilon\cdot(Z/c)^2, \qquad -\Delta^{\mathrm{rel}}\langle r\rangle/\langle r\rangle = \gamma_r\cdot(Z/c)^2 \quad \text{(A0)}$$

The γ are given for s, for $\mathrm{p}_{1/2}$, for $\mathrm{p}_{3/2}$, and for the average $\bar{\mathrm{p}} = {}^1/_3\cdot\mathrm{p}_{1/2} + {}^2/_3\cdot\mathrm{p}_{3/2}$ in Table 3, A, B, C, and D, respectively. (The γ values for ϵ (though $\Delta^{\mathrm{rel}}\epsilon/\epsilon^{\mathrm{norel}}$) for s and for $\bar{\mathrm{p}}$ were already presented in ref 8. However, those $\gamma_\epsilon(\bar{\mathrm{p}})$ are erroneous.) The valence s and $\mathrm{p}_{1/2}$ are relativistically contracted ($\gamma_r < 0$), and relativistically stabilized ($\gamma_\epsilon < 0$), except concerning the stabilization of $\mathrm{p}_{1/2}$ of the light electropositive atoms B and Al.

The valence $p_{3/2}$ is relativistically destabilized ($\gamma_\epsilon > 0$) and slightly expanded ($\gamma_r > 0$). The valence $\bar{p}$ average varies from destabilization and slight expansion to weak stabilization and weak contraction, when going in the periodic table from the upper left to the lower right. There is no strict correlation between energetic stabilization and spatial contraction.

Appendix II

Classical Localized Pictures in Quantum Mechanics. Because of Heisenberg's uncertainty, it is in principle forbidden to speak in quantum mechanics of a velocity or momentum value at a given position. However, one can still ask the following question: Given a specific integral representation for an expectation value, say for the energy or for the kinetic energy or for the momentum, which pieces of position space contribute most? Discussing such positional contributions of momentum to the energy helps to understand the physical mechanism in the given representation by well-defined mathematical formulas.

Furthermore, the mentioned caveat holds strictly only as long as the classical uncertainty limits are more restrictive than the quantum mechanical Heisenberg condition

$$\Delta x \cdot \Delta p = n \geq {}^{1}/_{2} \tag{A1}$$

where $n = {}^{1}/_{2}$ holds for a Gaussian distribution. A Gaussian reference state is used, for instance, to define the quasiclassical Husimi phase space function.[38] For an eigenstate in a smooth potential, n in eq A1 is of the order of the principal quantum number. Here we use atomic units, i.e., $\hbar = 1$, $m_e = 1$, $e = 1$.

Now, let Δx_{cl} be the uncertainty of a classical position measurement of an electron in an atom, at distance r from the nucleus (reasonably, with $r > \Delta x_{cl} > 0$); and let Δp_{cl} be its respective experimental momentum uncertainty. A classical model may then be used, if

$$\Delta x_{cl} \cdot \Delta p_{cl} \gg {}^{1}/_{2} \tag{A2}$$

For a valence electron with small energy, i.e., $\epsilon \approx 0$, the comparatively large kinetic and potential energies, T and V, approximately cancel each other, $-V \approx T$.[28] Note that for a one-electron orbital in a Hartree−Fock potential or any similarly screened Coulomb potential, the virial relation significantly differs from the relation for pure Coulomb potentials (a good approximation for any many-electron molecule and its total bond energy), where $-V = 2T$ holds. This important point is not always remembered by all authors.

In the nonrelativistic case,

$$T^{\mathrm{nonrel}} = p^2/2m, \text{ i.e., } p_{cl}{}^{\mathrm{nrel}}(r) = \sqrt{-2mV(r)} \tag{A3}$$

The Δp_{cl} corresponding to Δx_{cl} is then given by

$$\Delta p_{cl}{}^{\mathrm{nrel}} = |(dp(r)/dr)| \cdot \Delta x_{cl} = (m/p) \cdot |dV(r)/dr| \cdot \Delta x_{cl} \tag{A4}$$

In the relativistic case, we have

$$T^{\mathrm{rel}} + mc^2 = \sqrt{(m^2c^4 + p^2c^2)} \tag{A5}$$

$$p_{cl}{}^{\mathrm{rel}} = \sqrt{(-2mV + V^2/c^2)} \tag{A6}$$

yielding

$$\Delta \mathrm{p}_{cl}{}^{\mathrm{rel}} = (m/p) \cdot |dV/\mathrm{d}r| \cdot (1 - V/mc^2) \cdot \Delta x_{cl} \tag{A7}$$

For an electron near the nucleus, $m_e = 1$ and $-V \approx Z/r$. From eq A2 we then obtain for the nonrelativistic and relativistic cases, respectively,

$$Z \gg {}^{1}/_{2} \cdot p^{\mathrm{nrel}} \text{ and } Z \gg {}^{1}/_{2} \cdot p^{\mathrm{rel}}/(1 + Z/rc^2) \tag{A8}$$

This means for the nonrelativistic case that the classical model is applicable only for

$$r^{\mathrm{nrel}} \gg 1/2\mathrm{Z} \tag{A9}$$

Because the orbital radius is of the order of $<r> \sim n^2/\mathrm{Z}$, a classical orbit model is never applicable 'inside' an atom. However, in the relativistic case, eq A8 yields a smaller critical value $r^{\mathrm{rel}} < r^{\mathrm{nrel}}$, namely

$$r^{\mathrm{rel}} \gg [1 - (2Z/c)^2] + \sqrt{[1 - (2Z/c)^2]}/4\mathrm{Z} \tag{A10}$$

This reduction is bigger than the hydrogenic relativistic orbital contraction, i.e., a classical model becomes more reasonable in the relativistic case. For instance for any $Z > c/2 = 68.5$, eq A10 just means nothing else than the trivial restriction $r^{\mathrm{rel}} > 0$.

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