Theor Chim Acta (1991) 81: 139–155

Theoretica Chimica Acta

Relativistic bond lengthening of UO_2^{2+} and UO_2

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Received December 1, 1990/Received in revised form and accepted February 25, 1991

Summary. Relativistic calculations on UO_2 [1] have shown that relativity leads to substantial bond *lengthening* in this compound, in contrast to the bond contraction found almost exclusively for other compounds. The bond lengthening is *not* caused by the relativistic expansion of the $5f$ valence AO of U, which is the primary bond forming orbital on U in UO_2. The origin of the bond lengthening can be traced back to the semi-core resp. subvalence character of the U $6p$ AO. The valence character of $6p$ shows up in an increasing depopulation of the $6p$ upon bond shortening, and hence loss of mass-velocity stabilization. The core character of $6p$ shows up in large off-diagonal mass-velocity matrix elements $\langle 5p|h_{\mathrm{MV}}|6p\rangle$ which are shown to have an overall bond lengthening effect. The larger expansion in UO_2 than in UO_2^{2+} is due to destabilization of U levels in UO_2, caused by repulsion of the two additional $5f$ electrons.

The present analysis corroborates the picture of relativistic bond length effects of Ref. [2].

Key words: Relativistic bond lengthening – Mass-velocity effects – Uranium compounds

1. Introduction

Since the beginning of the 1970s there has been an increasing number of calculations including relativistic effects on atoms and molecules. For atoms the situation concerning the relativistic changes is clear: s and $p_{1/2}$ orbitals are stabilized and contract, d and f orbitals are destabilized and expand, while the behaviour of $p_{3/2}$ orbitals is intermediate [3–6]. In molecules the relativistic *contraction* of the bond length that is usually found, has initially been related to the contraction of the valence AOs involved in the bond (predominantly s and p) [4–7]. This explanation of relativistic bond length contraction in terms of AO contraction was questioned by Ziegler et al. [2], who obtained and interpreted the bond length contraction using a first order perturbation theoretical treatment of the relativistic effects [8, 9] within a density functional (Hartree–Fock–Slater) approach [10, 11]. To first order, relativistic changes of the wavefunction do not enter the total energy, and therefore it was not necessary to invoke AO contraction in this type of explanation of the bond length contraction. Other studies, using different computational approaches, corroborated these results [12–14].

The essence of the picture of relativistic bond lengthening of Ref. [2] is as follows (compare also [16]). Let us write for the bond energy of a diatomic system with non-relativistic harmonic force constant k and equilibrium bond length R_e:

$$\Delta E(R) \approx (1/2)k(R - R_e)^2 + \Delta E^1_{\mathrm{rel}} + \cdots . \tag{1}$$

This yields for the first order relativistic bond length change:

$$\Delta^1_{\mathrm{rel}} R = R_e^{\mathrm{rel}} - R_e^{\mathrm{nonrel}} \approx -k^{-1}[d\Delta E^1_{\mathrm{rel}}/dR]_{R_e^{\mathrm{nonrel}}} \tag{2}$$

where one alternative expression [16] is:

$$\begin{aligned} dE^1_{\mathrm{rel}}/dR &= d/dR\langle \Psi^{\mathrm{nonrel}}|h_{\mathrm{MV}} + h_{\mathrm{D}} + h_{\mathrm{SO}}|\Psi^{\mathrm{nonrel}}\rangle \\ &= \langle \Psi^{\mathrm{nonrel}}|d/dR(h_{\mathrm{MV}} + h_{\mathrm{D}} + h_{\mathrm{SO}})|\Psi^{\mathrm{nonrel}}\rangle \\ &\quad + \langle d\Psi^{\mathrm{nonrel}}/dR|h_{\mathrm{MV}} + h_{\mathrm{D}} + h_{\mathrm{SO}}|\Psi^{\mathrm{nonrel}}\rangle + \text{c.c.} \end{aligned} \tag{3}$$

It turns out that in general the most important term in dE^1_{rel}/dR is $d/dR\langle \Psi^{\mathrm{nonrel}}|h_{\mathrm{MV}}|\Psi^{\mathrm{nonrel}}\rangle$. It has been argued in Ref. [2] that this derivative is usually positive. Upon bond shortening the major contribution to the inner repulsive wall of the E versus R curve comes from kinetic energy increase due to the increasing Pauli repulsion of occupied valence orbitals on one atom with subvalence core orbitals on the other atom. The (negative) mass-velocity correction also increases, i.e. becomes more negative at shorter R, hence the positive $d\Delta E^1_{\mathrm{rel}}/dR$ (cf. [2] and Sect. 3 below).

It has been pointed out by Schwarz et al. [15–17] that one can, considering bond length change and relativity as two perturbations and using the interchange theorem of double perturbation theory [18], obtain an equally valid first order formulation of the relativistic bond length change in which the relativistic change of the wavefunction (in particular of the electron density) *does* enter. In this alternative formulation, the last line of Eq. (3) is to be replaced by:

$$\Delta^1_{\mathrm{rel}} R = \cdots - k^{-1} \int (dV_{\mathrm{ne}}/dR)\, \Delta^1_{\mathrm{rel}}\varrho \, dr. \tag{4}$$

Here the bond length change is related to the electrostatic Hellmann–Feynman force exerted by the relativistic change of the molecular electron density, $\Delta^1_{\mathrm{rel}}\varrho$, upon the nuclei. It is not yet completely clear if this formulation proves the traditional association of relativistic bond shortening with relativistic AO contraction correct. It is possible to split $\Delta^1_{\mathrm{rel}}\varrho$ into two parts, the sum of the atomic relativistic density changes and the change in the deformation density:

$$\Delta^1_{\mathrm{rel}}\varrho = \textstyle\sum_{\mathrm{at}} \Delta^1_{\mathrm{rel}}\varrho_{\mathrm{at}} + \Delta^1_{\mathrm{rel}}\varrho_{\mathrm{def}}. \tag{5}$$

It is not clear beforehand which one of the two parts yields the dominant contribution to the Hellmann–Feynman force. Most attention has been given to the atomic part and it has been concluded [15, 16] that this term is contracting resp. expanding if the valence AOs contract resp. expand. A direct relation would thus exist between AO contraction and bond length contraction, just as in the traditional view, if the atomic contribution is dominant. That would not be the case if the deformation density contribution were dominant. We will elsewhere discuss the explicit evaluation of these contributions to the Hellmann–Feynman force. Here we note that it is interesting to study systems for which relativistically *expanding* AOs make a major contribution to the bond. In the traditional view the bond should expand, whereas according to Ref. [2] contraction would still occur. Almost all of the systems studied to date have valence *s* and *p* AOs, which contract. These systems exhibit relativistic bond contraction, except for the somewhat special cases of Tl_2 [19a] and TlH^+ [19b], where spin-orbit coupling dominates. The early actinides, however, have expanding valence *5f* and *6d* AOs. An investigation of the electronic structure of the actinocenes $Ac(COT)_2$ [20] showed important *6d* and *5f* contributions to the bonding. In spite of the valence AO expansion, the relativistic effect on the bond length was contraction. Recently, however, calculations on UO_2 [1], where *f* orbitals are important for the bonding, showed the first – in addition to the above-mentioned Tl compounds – well-documented relativistic bond length expansion.

These last two results appear to be contradictory, which prompted us to carry out a detailed investigation into the relativistic effects on the bond length of UO_2^{2+} and UO_2. Non-relativistic and relativistic calculations are reported on UO_2^{2+} and UO_2. We have calculated the non-relativistic bond energy and the relativistic correction to it for a number of distances in order to understand the relativistic expansion of the molecules. The bond length expansion can be explained by rather intricate features of the electronic structure of the title molecules, without reference to the expansion of the *5f* U AO.

The paper is organized as follows. In Sect. 2 we briefly discuss the computational method used and give a discussion of the electronic structure features of UO_2^{2+} and UO_2 that are relevant for the analysis of the relativistic bond lengthening. This analysis is given in Sect. 3. Section 4 contains the conclusions.

2. The electronic structure of UO_2^{2+} and UO_2

Electronic structure calculations have been carried out using the simplest density-functional approach, $X\alpha$ or Hartree–Fock–Slater (HFS). The HFS computational method used [10, 11] is characterized by the use of a density fitting procedure to obtain an accurate Coulomb potential, by accurate numerical integration of the effective one-electron hamiltonian matrix elements [21], and by the possibility to freeze core orbitals. The (*1s*-*5s*), (*2p*-*5p*), (*3d*-*5d*), and *4f* orbitals on U and the *1s* orbital on O have been frozen. The valence basis was double-ζ for the U *6s*, *6p* and *7s*, triple-ζ for *5f* and *6d* and double-ζ for the O *2s* and *2p*. A single *7p* on U and *3d* on O were added as polarization functions.

There have been many studies on the uranyl ion UO_2^{2+} [1, 22–31], important issues being the linearity of the O-U-O system and the character of the HOMO. In both cases the U *6p* orbital plays a crucial role, as pointed out a.o. by Tatsumi and Hoffmann [24] and by Jørgensen [22, 25]. One would expect the bonding interactions to be primarily the σ and π interactions of O *2p* with U valence *5f* and *6d*. This expectation is borne out by the analysis of the orbital compositions (Table 1), cf. also the Mulliken AO populations of (for UO_2^{2+}) $(2p)^{4.0}(5f)^{3.3}(6d)^{0.9}$. The picture is however complicated by the strong interaction of O *2s* and *2p* with the filled U *6p* shell. The U *6p* orbital cannot be considered a core orbital, since it has a fairly high energy (comparable to O *2s*) and is spatially even more extended than the valence *5f* orbital. The interaction

Table 1a. Population analysis for orbitals of UO_2^{2+} for U-O distance of 3.25 a.u.

	Orbital		Atomic composition (%)							
Orbital	character	Eigenvalue (e.V.)	U 5*f*	U 6*s*	U 6*p*	U 6*d*	U 7*s*	U 7*p*	O 2*s*	O 2*p*
Unoccupied orbitals										
$4\sigma_u$	2*p*-6*p* anti-b.	−11.47	29		21			1	2	46
$3\pi_u$	5*f*-2*p* anti-b.	−18.30	55		1					43
$1\delta_u$	5*f*	−21.47	100							
$1\phi_u$	5*f*	−22.01	100							
Occupied orbitals										
$3\sigma_u$	5*f* (−2*p* bonding)	−22.85	71		11				1	17
$3\sigma_g$	O 2*p* (−6*d* bonding)	−23.04		3		15	2		7	74
$1\pi_g$	O 2*p* (−6*d* bonding)	−23.83				15				85
$2\pi_u$	5*f*-2*p* π-bonding	−23.89	46		3					50
$2\sigma_u$	6*p*-2*s* anti-b., −2*p* b.	−29.17	−1		35			−3	51	18
$1\pi_u$	$6p_\pi$	−34.27			95					4
$2\sigma_g$	2*s* (−6*s* anti-b.)	−36.20		16		3	−3		85	−1
$1\sigma_u$	2*s*-6*p* bonding	−43.12	2		31			−2	56	11
$1\sigma_g$	6*s* (−2*s* bonding)	−49.49		79					14	6
Gross populations			3.3	2.0	5.5	0.9	0.0	−0.1	2.2	4.0

Table 1b. Population analysis for orbitals of UO_2 for U-O distance of 3.25 a.u.

	Orbital		Atomic composition (%)							
Orbital	character	Eigenvalue (e.V.)	U 5*f*	U 6*s*	U 6*p*	U 6*d*	U 7*s*	U 7*p*	O 2*s*	O 2*p*
Unoccupied orbitals										
$4\sigma_u$	7*p*	3.04	7		1			98	−5	−1
$3\pi_u$	5*f*-2*p* anti-b.	−0.41	67		1			11		20
Singly occupied orbitals										
$1\phi_u$	5*f*	−1.40	100							
$1\delta_u$	5*f*	−1.81	100							
Doubly occupied orbitals										
$3\sigma_u$	5*f* (−2*p* bonding)	−4.93	63		20			3		15
$2\pi_u$	2*p*-5*f* π-bonding	−6.95	26		8			−1		67
$3\sigma_g$	O 2*p* (−6*d* bonding)	−7.29		4		15	5		3	72
$1\pi_g$	O 2*p* (−6*d* bonding)	−7.97				16				84
$2\sigma_u$	6*p*-2*s* anti-b., −2*p* b.	−13.15	−1		30			−1	44	28
$1\pi_u$	U $6p_\pi$	−16.33			91					7
$2\sigma_g$	2*s* (−6*s* anti-b.)	−19.54		20		3	−2		80	−1
$1\sigma_u$	2*s*-6*p* bonding	−26.47	2		28			−2	60	10
$1\sigma_g$	6*s* (−2*s* bonding)	−31.48		72					20	7
Gross populations			4.3	2.0	5.5	1.0	0.1	0.1	2.0	4.5

with the O orbitals squeezes ~0.5 electron out of the U 6*p*. The details of the various interactions, leading to the level scheme and orbital compositions given in Table 1, are as follows.

Considering first UO_2^{2+} (Table 1a) we observe that the $1\sigma_g$ (mostly U 6*s*) and $2\sigma_g$ (mostly O 2*s*) orbitals show mixing of U 6*s* with O 2*s*: a four electron destabilizing interaction. In σ_u symmetry the interaction of $6p\sigma$ and $5f_{z^3}$ $(=5f\sigma)$

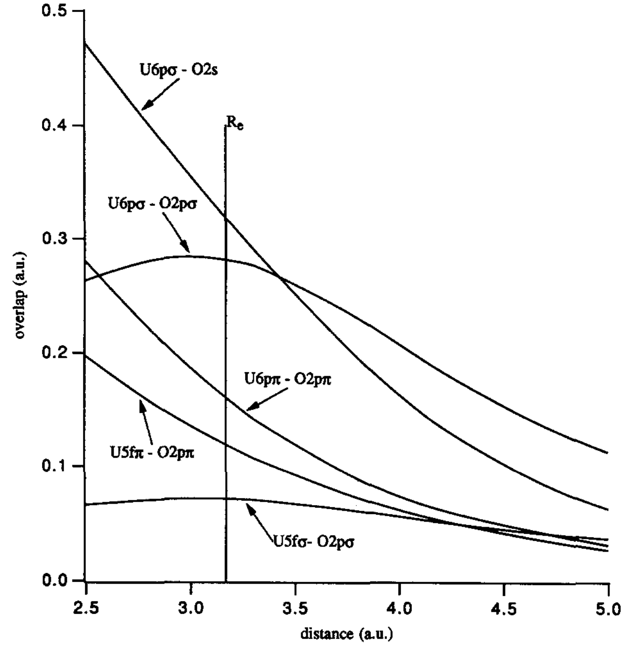


Fig. 1. Overlaps between various U and O atomic orbitals as function of the U-O distance

with O $2p\sigma$ is of particular interest. It has already been stressed that the interaction between U $6p\sigma$ and O $2p\sigma$ is very strong [24]. It is interesting in this connection to compare the overlaps between the relevant orbitals, which are given in Fig. 1 as a function of the U-O distance. Figure 1 shows that the overlap of O $2p\sigma$ with U $6p\sigma$ is very much larger than with U $5f\sigma$. Since the U-O equilibrium distance is rather short ($\sim$3.2 a.u.), a large splitting between the bonding and antibonding U $6p\sigma$/O $2p\sigma$ combinations results. The antibonding combination is in fact high up in the virtual spectrum, above the $5f$ orbitals (it becomes the $4\sigma_u$). The (smaller) interaction of O $2p\sigma$ with $5f\sigma$ causes the $4\sigma_u$ to push the $5f\sigma$ orbital down from the $5f$ manifold (to be identified with the

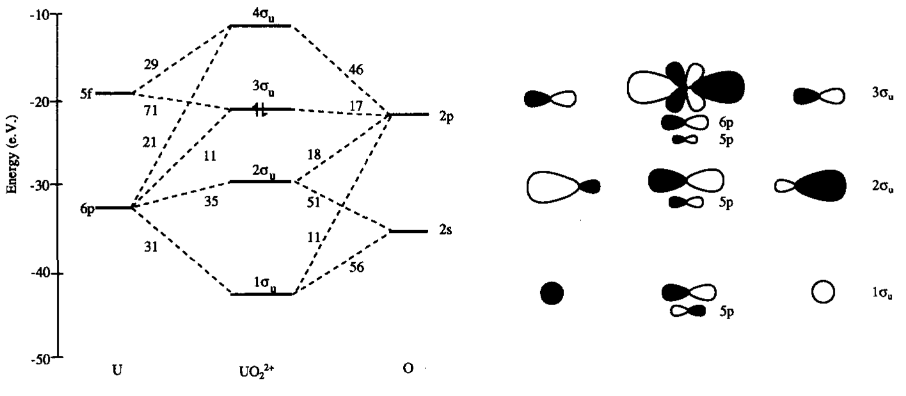


Fig. 2. Interaction diagram for the σ_u levels. The percentage contribution of an AO to an MO (based on Mulliken gross populations) is given alongside the corresponding interaction line

position of the 100% $5f$ orbitals $1\phi_u$, $1\delta_u$). The resulting $3\sigma_u$, which has 60–70% $5f\sigma$ character, becomes the HOMO. The bonding U $6p\sigma$/O $2p\sigma$ combination is stabilized and interacts strongly, in a four electron repulsive interaction, with the σ_u combination of O $2s$ (cf. Fig. 1): the resulting $1\sigma_u$ and $2\sigma_u$ orbitals are split by ca. 14 eV. The $2\sigma_u$, which would, on account of its U $6p\sigma$/O $2p\sigma$ bonding character, be expected to be below the almost noninteracting $6p\pi_u$ (the $1\pi_u$ MO), is in fact pushed considerably above $1\pi_u$ by O $2s$. The whole level pattern of $1\sigma_u$-$4\sigma_u$ orbitals and their composition is given in Fig. 2. For future reference pictures of the orbitals are given with the phase with which the U $5p$ core orbital is admixed explicitly indicated.

As for the other orbitals, the $2\pi_u/3\pi_u$ pair is obviously the pair of bonding/antibonding $5f\pi_u$/O $2p\pi_u$ orbitals. This suggests that the major contribution to the U-O bond comes from the π bonding between U $5f$ and O $2p$. The *gerade* combinations of O $2p\pi$ and O $2p\sigma$ ($1\pi_g$ and $3\sigma_g$) reveal some stabilizing contribution from U $6d$ admixture.

We wish to draw attention to a few special features of the electronic structure that will prove important in the analysis of the relativistic bond lengthening. In Table 2 the gross populations (2a) and net populations (2b) of relevant AOs are given for a number of U-O distances. The presence of U $6p\sigma$ character in the virtual spectrum (cf. $4\sigma_u$ in Table 1a) implies that the U $6p\sigma$ gross population drops below 2.0: *there is a* U $6p$ "*hole*". This hole has been noted by Pyykkö and Lohr [27] and has been related by Pyykkö to NQR data [32]. In our calculations the hole is clearly visible in the gross populations and *increases at shorter distances*. At R_e the gross population of U $6p\sigma$ is 1.53, so there is (with this definition in terms of Mulliken gross population) a hole of 0.47 electron. (Pyykkö and Lohr found a hole of 0.16 electron in their Extended Hückel

Table 2a. Gross populations for some AOs of U and O in UO_2^{2+} at various U-O distances

	Σ_u symmetry				Π_u symmetry			Σ_g symmetry	
Distance	U $6p\sigma$	U $5f\sigma$	O $2p\sigma_u$	O $2s\sigma_u$	U $6p\pi_x$	U $5f\pi_x$	O $2p\pi_{u,x}$	U $6s$	O $2s\sigma_g$
2.50	0.95	1.51	1.19	2.45	1.86	0.97	1.17	1.78	2.09
3.00	1.36	1.51	1.04	2.27	1.94	0.92	1.12	1.93	2.11
3.50	1.69	1.41	0.87	2.14	1.98	0.94	1.06	1.96	2.12
4.00	1.87	1.25	0.86	2.07	1.99	1.03	0.96	1.98	2.09
4.50	1.94	1.09	0.94	2.04	1.99	1.17	0.82	1.99	2.05

Table 2b. Net populations for some AOs of U and O in UO_2^{2+} at various U-O distances

	Σ_u symmetry				Π_u symmetry			Σ_g symmetry	
Distance	U $6p\sigma$	U $5f\sigma$	O $2s\sigma_u$	O $2p\sigma_u$	U $6p\pi_x$	U $5f\pi_x$	O $2p\pi_{u,x}$	U $6s$	O $2s\sigma_g$
2.50	1.93	1.31	3.83	0.98	1.98	0.71	1.12	2.49	2.62
3.00	1.84	1.37	3.04	0.84	1.98	0.74	1.02	2.30	2.44
3.50	1.92	1.32	2.52	0.73	1.99	0.82	0.95	2.20	2.33
4.00	1.98	1.18	2.25	0.76	1.99	0.95	0.87	2.09	2.22
4.50	2.00	1.04	2.13	0.87	1.99	1.11	0.76	2.03	2.13

calculation.) The table with net populations (2b) shows that the net population differs significantly from the gross population. This is a simple consequence of the large overlaps mentioned before, which cause considerable (negative) contributions to the gross population to come from overlap populations. The table with net populations also shows that in a number of cases these populations are (much) larger than 2.0 (notably O $2s\sigma_u$ and U $6s$). Such high net populations again arise from large overlaps: the coefficients in the antibonding orbitals become large due to the normalization factor $(1/\sqrt{(2-2S)}$ in the symmetrical case; note the larger amplitudes drawn in Fig. 2 for $2\sigma_u$ versus $1\sigma_u$). The negative overlap population in the antibonding orbital is (much) larger than the positive overlap population in the bonding orbital, the total net population is accordingly larger than 2.0 with a relatively large contribution from the antibonding orbital. These effects are pronounced here due to the short U-O distance c.q. large overlaps and will prove to play a key role in the relativistic bond lengthening.

The overlaps in symmetry π_u are much smaller (cf. Fig. 1). Therefore the hole effect, which is also present in π_u symmetry, is much smaller: at R_e the hole is only 0.07 e.

Next we will briefly discuss UO_2, which has, compared with UO_2^{2+}, two extra electrons in the empty 1δ, 1ϕ orbitals above $3\sigma_u$. (The configuration $(1\delta_u)^1(1\phi_u)^1$ is most stable, which relativistically corresponds to $(3j_{3/2}u)^1(1j_{5/2}u)^1$, see Ref. [1].) Of course going from a 2+ to a neutral species first of all shifts all levels upwards. The second effect is the relatively strong upward shift of the $5f$ levels due to the large $5f$-$5f$ repulsion of the tight $5f$ orbital (note the additional electrons are in pure $5f$ orbitals). As a consequence, the gap between the $1\phi_u$, $1\delta_u$ levels and the $3\sigma_u$ widens considerably (see Table 1b). In the $2\pi_u/3\pi_u$ pair the lower bonding orbital is no longer a fifty/fifty mixture of O $2p_\pi$ and U $5f_\pi$, but has more pronounced O $2p$ character. It is not even stabilized below the O $2p3\sigma_g$ and $1\pi_g$, as it was in UO_2^{2+}. The U $5f$-O $2p$ π bond is therefore probably weaker. Since the repulsive effects in the lower levels between the occupied U $6s$, $6p$ and O $2s$ do not seem to be much different from UO_2^{2+}, the bond length may be expected to be longer, as indeed it is (cf. Table 3). In the upper part of the spectrum the U $7p$ is now below the antibonding U $5f\sigma$/O $2p\sigma_u$ combination and has become the $4\sigma_u$. The $6p$ holes are 0.43 e for $6p\sigma$ and 0.02 e for $6p\pi$ at R_e. This is slightly smaller than for UO_2^{2+}, but in UO_2 the hole increases faster on going to shorter U-O distance.

Up to this point only non-relativistic calculations have been considered. The relativistic corrections to the levels have been discussed extensively elsewhere [31] and are not given here. We do give, however, a table with atomic relativistic corrections (Table 4) which will be needed in the next section. Note the large

Table 3. Calculated non-relativistic and relativistic bond-distances (in bohr) and force constant (in mdyn/Å) for UO_2^{2+} and UO_2

	UO_2^{2+}	UO_2
R_e non-relativistic	3.163	3.326
R_e relativistic (1st order)	3.191	3.464
R_e relativistic (quasi-)	3.213	3.466
Expansion (1st order) in %	0.89	4.15
k (non-relativistic)	19.3	13.1

Table 4. Relativistic corrections for orbitals of U atom. Energies are given in e.V. Δ_{MV}: mass-velocity; Δ_{DAR}: Darwin; Δ_{SO}: spin-orbit; Δ_{POT}: potential correction due relativistic change in electron density

Orbital	E_{NREL}	Δ_{MV}	Δ_{DAR}	Δ_{SO}	Δ_{POT}	E_{REL}	Spinor
5*s*	−240.1	−164.20	93.14	−27.32	21.46	−317.00	$s_{1/2}$
5*p*	−190.97	−33.51	−0.20	−38.58	20.61	−242.66	$p_{1/2}$
		−33.51	−0.20	12.21	20.61	−191.86	$p_{3/2}$
6*s*	−35.29	−32.43	18.35	−4.01	5.05	−47.81	$s_{1/2}$
6*p*	−21.65	−5.54	−0.03	−5.72	4.71	−28.23	$p_{1/2}$
		−5.54	−0.03	2.02	4.71	−20.49	$p_{3/2}$
6*d*	−3.13	−0.68	−0.01	−0.38	2.18	−2.02	$d_{3/2}$
		−0.68	−0.01	0.08	2.18	−1.52	$d_{5/2}$
5*f*	−8.88	−1.13	−0.03	−1.04	8.44	−2.63	$f_{5/2}$
		−1.13	−0.03	−0.36	8.44	−1.95	$f_{7/2}$

Off-diagonal element $\langle 5p|h_{\mathrm{MV}}|6p\rangle = 13.63$ e.V.

mass-velocity (MV) terms for U 6*p* and U 5*p*. The U 6*p* is already sufficiently core-like to have a large mass-velocity correction, but of course the U 5*p* has a much larger mass-velocity correction still, and even the off-diagonal term, $\langle 5p|h^1_{\mathrm{MV}}|6p\rangle$, is quite large. It is a special feature of the U atom that it has, apart from the true 5*s*, 5*p* core shell, also the 6*s*, 6*p* shell which has both core-like features (large MV terms) and valence character (high energy, large radius).

3. Relativistic bond lengthening in UO_2^{2+} and UO_2

Calculations on UO_2^{2+} and UO_2 were done for a number of U-O distances, both non-relativistically and including first order relativistic corrections. As noted before [1], second order relativistic effects are large and quasi-relativistic calculations of the type described in Ref. [33], which include certain types of higher order corrections, are to be preferred for elements as heavy and relativistic as U. Such quasi-relativistic calculations have been performed on UO_2^{2+} and UO_2 and yield results for the bond lengthening that differ little from those obtained in first order, as can be seen in Table 3. For purposes of analysis we may therefore focus on the first order calculations. Non-relativistic bond-energy curves, and those including the first order relativistic corrections are given in Fig. 3. The equilibrium distances of UO_2^{2+} and UO_2 are given in Table 3. The relativistic curves are destabilized and show equilibrium bond lengths larger than the non-relativistic ones. The expansion of UO_2 (4%) is much larger than the expansion of UO_2^{2+} (1%). The expansion of UO_2 of 0.14 a.u. is close to the value found by Allen et al. [1]. Our equilibrium bond length is smaller. Since the only difference with the calculations in Ref. [1] is a larger basis set, in particular the addition of polarization functions on the oxygens, the present shorter bond lengths provide another example of the well-known bond shortening effect of these polarization functions (cf. [34] for CO). Note that the weaker bonding in UO_2 anticipated in the previous section shows up in the more shallow bond energy curve of Fig. 3. To some extent this explains the difference in expansion between UO_2^{2+} and UO_2 (smaller k in Eq. (2)).

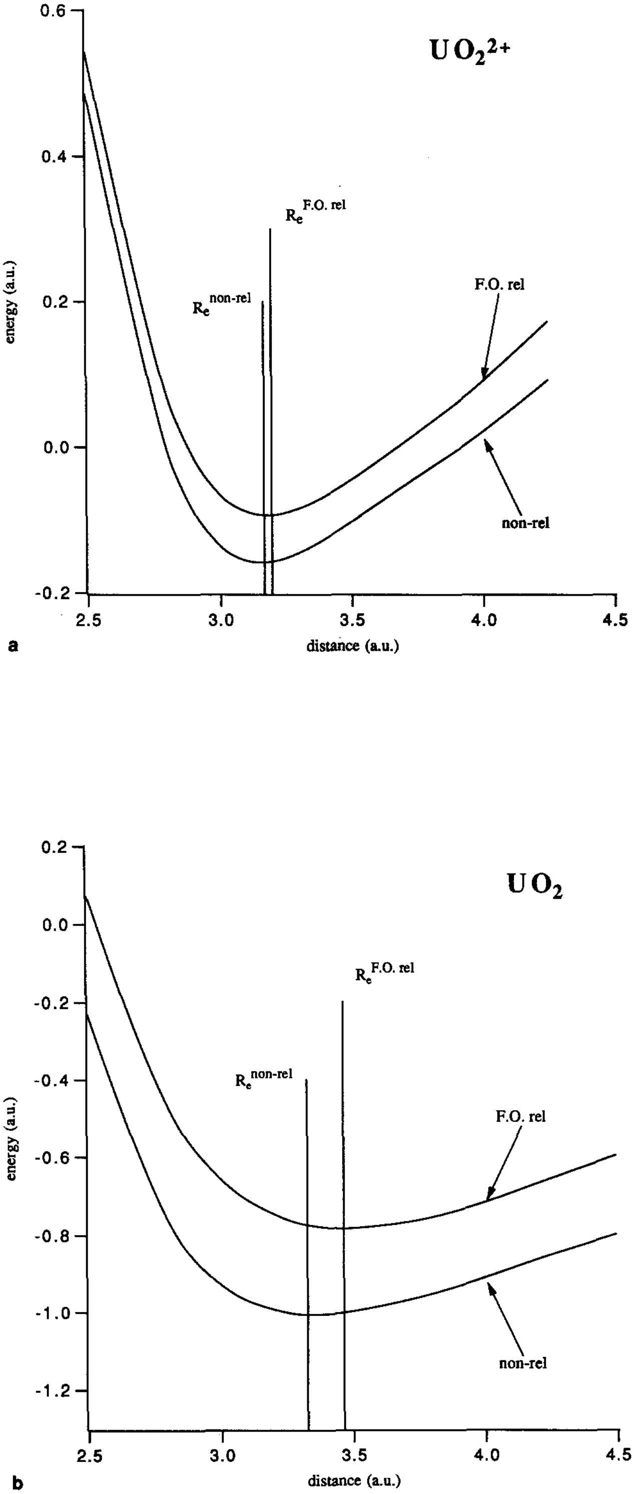


Fig. 3. **a** Energy versus R for UO_2^{2+}. **b** Energy versus R or UO_2

Before discussing the uranyl case, we first briefly review the explanation of the relativistic contraction given in previous studies on e.g. AuH, AuCl, Au_2 [2]. Suppose we have a heavy atom A (with core) and a light atom B (no core, for simplicity), the bonding being between the valence orbitals ϕ_A^v and ϕ_B^v. Due to core-valence orthogonality, the core orbitals of A mix into the valence orbital of B. For properties such as $\langle T\rangle$ and $\langle h_{MV}\rangle$, only the admixing of the subvalence core orbital of A, ϕ_A^c, is important (see below). The molecular orbitals are then given by:

$$\phi_{\text{bond}} = c_A\phi_A^v + c_B(\phi_B^v - a\phi_A^c) \qquad \phi_{\text{anti-bond}} = c_A^*\phi_A^v - c_B^*(\phi_B^v - a\phi_A^c), \tag{6}$$

where a is the coefficient with which the core-orbital ϕ_A^c has to mix into ϕ_B^v to ensure orthogonality on the core of A ($a \sim \langle\phi_B^v\,|\,\phi_A^c\rangle$). The superscript * denotes the antibonding orbital. In general the coefficients of the antibonding orbital are larger than those of the bonding one: $|c^*| > |c|$, e.g. for a homonuclear molecule: $\sqrt{(1/(2-2S))} > \sqrt{(1/(2+2S))}$, with S the overlap of the atomic orbitals.

In the systems studied to date, typically only the bonding combination ϕ_{bond} was occupied. If the bond length is shortened, ϕ_A^c is more strongly admixed, because the overlap of ϕ_A^c with ϕ_B^v increases. This leads non-relativistically to a rise in kinetic energy (kinetic repulsion).

The mass-velocity effect:

$$\langle\phi|h_{MV}|\phi\rangle = -\langle\phi|\mathrm{p}^4|\phi\rangle/8m^2c^2 = -\langle\nabla^2\phi|\nabla^2\phi\rangle/8m^2c^2, \tag{7}$$

is definite negative and increases when $\langle T\rangle$ increases (classically the MV term is $-T^2/2c^2$). In the MO picture this effect arises from the diagonal core orbital contribution to the mass-velocity correction for the bonding MO:

$$\begin{aligned}\langle\phi_{\text{bond}}|h_{MV}|\phi_{\text{bond}}\rangle &= c_A^2\langle\phi_A^v|h_{MV}|\phi_A^v\rangle + 2c_Ac_B\langle\phi_A^v|h_{MV}|\phi_B^v\rangle + c_B^2\langle\phi_B^v|h_{MV}|\phi_B^v\rangle\\ &\quad - 2c_B^2a\langle\phi_B^v|h_{MV}|\phi_A^c\rangle - 2c_Ac_Ba\langle\phi_A^v|h_{MV}|\phi_A^c\rangle + c_B^2a^2\langle\phi_A^c|h_{MV}|\phi_A^c\rangle.\end{aligned} \tag{8}$$

Usually the diagonal core contribution (the last term on the second line) is very much larger than any other term. The coefficient a in this term increases on shortening the A-B distance since the overlap of ϕ_B^v with ϕ_A^c increases, whereas the coefficient c_B changes much more slowly. Therefore the diagonal core contribution causes the mass-velocity correction to become increasingly more negative: it relaxes the kinetic repulsion. The ensuing bond contraction can be quite large: AuH: 0.23 and Au_2: 0.46 Å [2].

We have singled out the diagonal core term with ϕ_A^c being *the upper core orbital* as the most important term for both kinetic repulsion (for which Eq. (8) applies with h_{MV} replaced with T) and its mass-velocity reduction. More deep-lying core orbitals will have (much) larger T and h_{MV} matrix elements, but are in general so tight that the overlap with ϕ_B^v becomes very small and therefore the a^2 factor reduces the corresponding $c_B^2a^2\langle\phi_A^c|h_{MV}|\phi_A^c\rangle$ term to insignificance. Numerical evidence will be provided below.

In order to understand the relativistic effect in uranyl, the above analysis has to be extended. If we associate U $6p$ with the valence orbital ϕ_A^v, it should be realized that this orbital has some core character in the sense that its diagonal MV matrix element is not negligible, and neither is the off-diagonal matrix element with the true core orbital (U $5p$). Moreover, U $6p$ is sufficiently deep-lying that also *anti*bonding orbitals involving U $6p$ are occupied. The combination of these factors leads to bond lengthening MV effects in the following way.

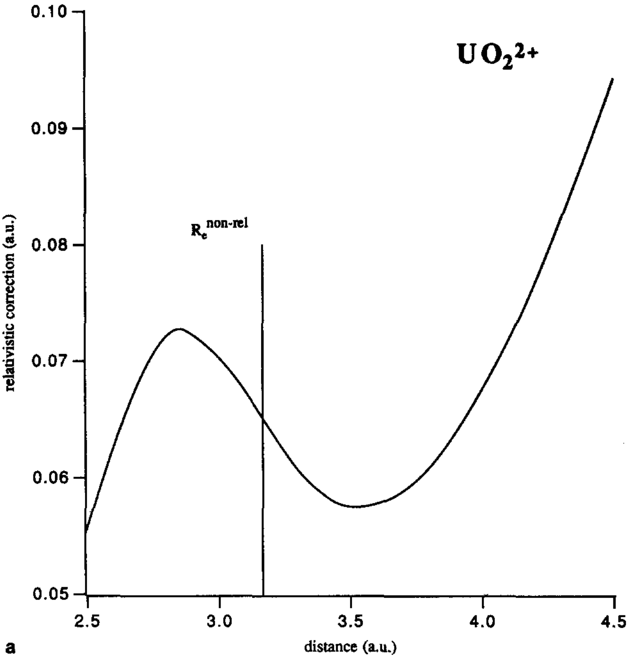
First, the diagonal term $c_A^2\langle\phi_A^v|h_{MV}|\phi_A^v\rangle$ (first term on right hand side of Eq. (8)) yields negative contributions in all occupied orbitals. If the sum of these contributions becomes less negative when R(U-O) decreases, this term has a bond lengthening effect. Shortening the U-O distance does indeed decrease the total negative contribution since less U 6*p* character remains in the occupied orbitals. This is clear from the increasing 6*p* hole noted before (note that the net population directly reflects this term with h_{MV} replaced with the unit operator). In the second place, the contribution of the off-diagonal term $-2c_Ac_Ba\langle\phi_A^v|h_{MV}|\phi_A^c\rangle$ has to be taken into account. The recent results of Schwarz et al. [35] enable us to establish the sign of this contribution. It has been shown in Ref. [35] that the mass-velocity matrix elements originate from the innermost core wiggle of the AOs in the matrix element, i.e. the 2*p* wiggle for a matrix element between 6*p* and 5*p*. If we take the phases of the 6*p* and 5*p* orbitals such that the outer lobes are positive in the positive *z* direction – as is assumed when we take c_A and c_B and a all positive in Eq. (6) – the inner 2*p* wiggles of the two orbitals have opposite phase, and the matrix element will be positive instead of negative. The overall minus sign of this term in a bonding orbital makes it negative again. Since the off-diagonal term scales with a, i.e. increases upon shortening R(U-O), it contributes to the contraction. However, for an *anti*bonding orbital the off-diagonal term will be $+2c_A^*c_B^*a\langle\phi_A^v|h_{MV}|\phi_A^c\rangle$, which is positive. This off-diagonal contribution in an antibonding orbital is therefore expanding and is rather important for two reasons. First, its derivative w.r.t. R scales as da/dR, not as the smaller $2a\,da/dR$ (the behaviour of the diagonal core contribution). Second, the coefficients (c_A^*, c_B^*) are larger than in the bonding orbital, particularly when the overlaps are large.

The overall result when ϕ_{bond} and $\phi_{\text{anti-bond}}$ are both occupied, depends on the relative importance of the individual mass-velocity elements. Expanding contributions have however been identified and will, if they dominate, lead to relativistic bond lengthening.

We now examine the uranyl case. The calculated first order corrections (sum of MV and Darwin) to the bond energy are given in Fig. 4a,b. For UO_2^{2+} we see in Fig. 4a the normal decrease with decreasing R(U-O) in the beginning and at the end of the curve. But in the range 3.5–2.7 bohr the curve rises, and this region is the most important one, because it includes the non-relativistic R_e. The derivative $d\,\Delta E_{\text{rel}}^1/dR$ is obviously negative at R_e, causing relativistic expansion of the molecules. The curve for UO_2 in Fig. 4b shows this anomalous behaviour more strongly (the derivative $d\Delta E_{\text{rel}}^1/dR$ is more negative) and over a larger distance range. The relatively large expansion in UO_2 is therefore caused by both a smaller k and a larger $d\Delta E_{\text{rel}}^1/dR$.

The relativistic correction has been split into contributions from different symmetries by simply summing the first order corrections over the occupied orbitals of a given symmetry. The result is given in Fig. 5. The two symmetries that are responsible for the negative slope of ΔE_{rel}^1 around R_e are σ_u and π_u. Symmetry π_g shows the "normal" contracting behaviour, whereas σ_g also exhibits some anomalous behaviour, but only at shorter distances than are relevant here. The *ungerade* symmetries are therefore singled out for closer scrutiny. It turns out that in these symmetries the mass-velocity effect is dominating, as before [2]. From now on only mass-velocity results are given.

In Table 5a the contributions per σ_u orbital to $-k^{-1}\,d\Delta E_{\text{rel}}^1/dR$ are given for the various terms specified in Eq. (8). The diagonal valence contribution $c_A^2\langle\phi_A^v|h_{MV}|\phi_A^v\rangle$ corresponds to the term $\langle 6p|6p\rangle$. This term is positive



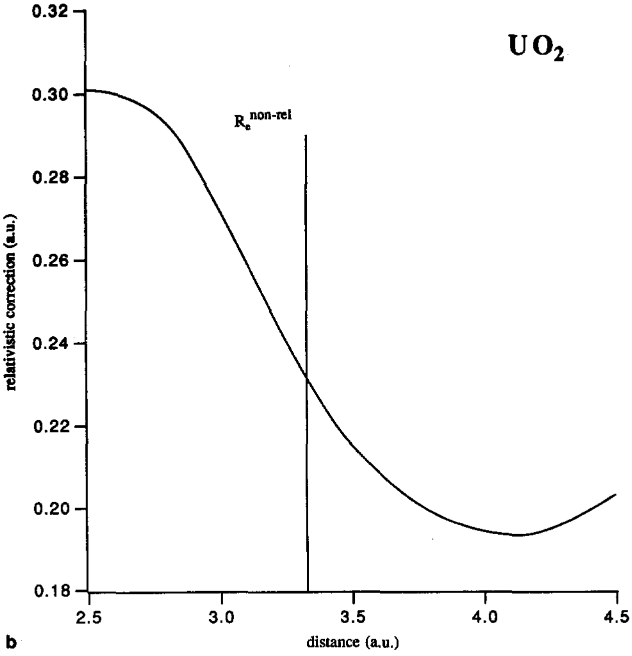


Fig. 4. **a** The total first-order relativistic energy correction for UO_2^{2+}. **b** The total first-order relativistic energy correction for UO_2

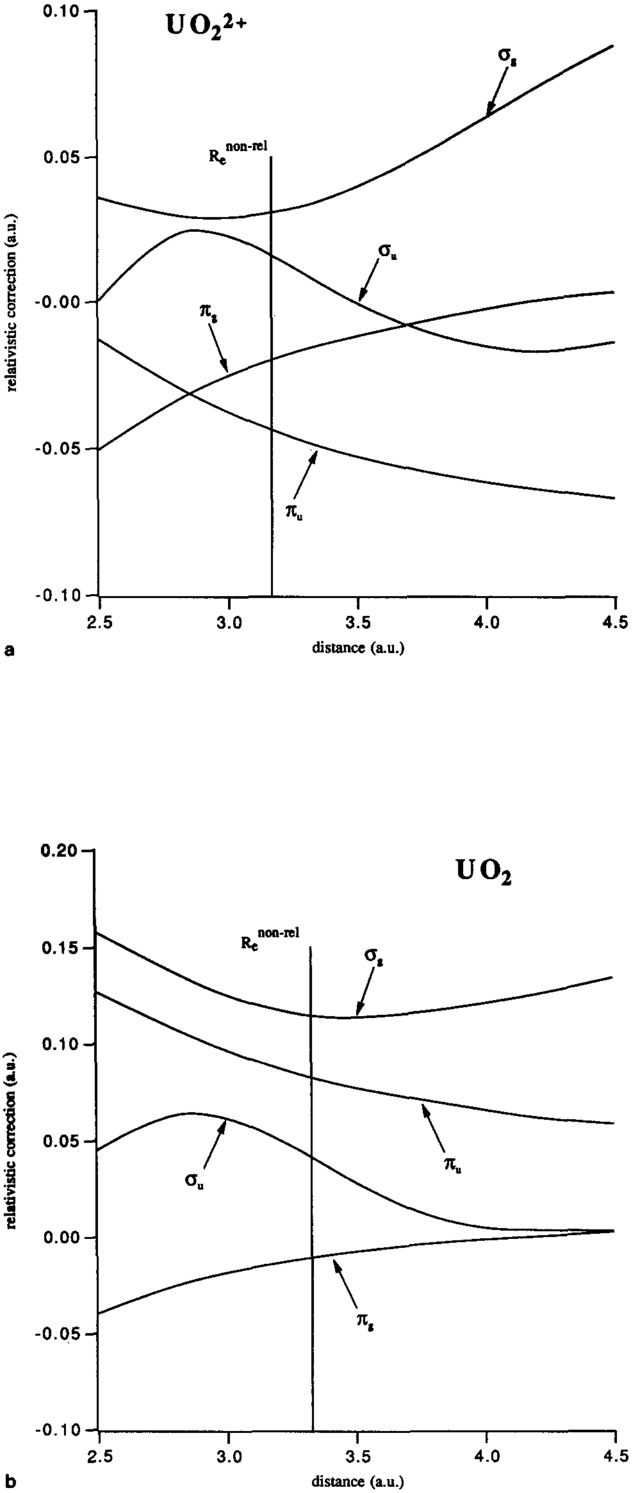


Fig. 5. a Contributions in various symmetries to the first order relativistic energy correction for UO_2^{2+}. **b** Contributions in various symmetries to the first order relativistic energy correction for UO_2

Table 5a. The most important mass-velocity contributions to the approximate bond length change $-k^{-1}\, dE^{1}_{\mathrm{rel}}/dR$ for symmetry σ_u. The derivative has been approximated by a finite difference at $R = 3.5$ and 3.0 bohr

		UO_2^{2+}	UO_2
$1\sigma_u$:	$\langle 6p\|6p\rangle$	0.0368	0.0581
	$\langle 5p\|5p\rangle$	−0.0376	−0.0626
	$\langle fp\|6p\rangle$	−0.0735	−0.1005
$2\sigma_u$:	$\langle 6p\|6p\rangle$	0.1189	0.2126
	$\langle 5p\|5p\rangle$	−0.0079	−0.0002
	$\langle 5p\|6p\rangle$	0.0361	−0.0031
$3\sigma_u$:	$\langle 6p\|6p\rangle$	−0.0815	−0.0955
	$\langle 5p\|5p\rangle$	−0.0090	−0.0200
	$\langle 5p\|6p\rangle$	0.0589	0.1040
sum:	$\langle 6p\|6p\rangle$	0.0742	0.1752
	$\langle 5p\|5p\rangle$	−0.0545	−0.0828
	$\langle 5p\|6p\rangle$	0.0215	0.0004
	total	0.0412	0.0928
	total MV σ_u:	0.0413	0.0869

Table 5b. The most important mass-velocity contributions to the approximate bond length change $-k^{-1}\, dE^{1}_{\mathrm{rel}}/dR$ for symmetry π_u. The derivative has been approximated by a finite difference at $R = 3.5$ and 3.0 bohr

		UO_2^{2+}	UO_2
$1\pi_u$:	$\langle 6p\|6p\rangle$	0.1571	0.3205
	$\langle 5p\|5p\rangle$	−0.0006	−0.0009
	$\langle 5p\|6p\rangle$	−0.0516	−0.0914
$2\pi_u$:	$\langle 6p\|6p\rangle$	−0.1397	−0.2705
	$\langle 5p\|5p\rangle$	−0.0055	−0.0095
	$\langle 5p\|6p\rangle$	0.0552	0.1048
	$\langle 5f\|5f\rangle$	0.0116	−0.0033
sum:	$\langle 6p\|6p\rangle$	0.0174	0.0500
	$\langle 5p\|5p\rangle$	−0.0061	−0.0104
	$\langle 5p\|6p\rangle$	0.0036	0.0134
	$\langle 5f\|5f\rangle$	0.0116	−0.0033
	total	0.0265	0.0497
	total MV π_u:	0.0239	0.0445

(expanding) in $1\sigma_u$ and $2\sigma_u$, which corresponds to loss of $6p$ character in these orbitals when the bond length is shortened. This $6p$ character is regained partly in $3\sigma_u$, but not completely as some $6p$ character builds up in the virtual spectrum, notably the $4\sigma_u$. There is a net expanding contribution from the $\langle 6p|6p\rangle$ terms, corresponding to the increasing $6p$ hole at shorter distances. The diagonal core contributions $\langle 5p|5p\rangle$ have the normal contracting behaviour.

They are, however, not much larger than the $\langle 6p|6p \rangle$ contributions, although the mass-velocity matrix element (Table 4) itself is very large (we return to this point below). Still, they cancel much of the $\langle 6p|6p \rangle$ contribution. For that reason the off-diagonal $\langle 5p|6p \rangle$ terms are important. They behave as predicted, contracting in the bonding orbital $1\sigma_u$, where $6p\sigma$ and $5p\sigma$ have opposite phase, and expanding in the upper two orbitals where the phases are equal (cf. Fig. 2). The net contribution is expanding. For neutral UO_2 the $6p$ hole formation is relatively more important, which fits in with the destabilization of the U AOs because of the two additional $5f$ electrons.

In the π_u symmetry (Table 5b) the picture is analogous, the loss of $6p$ character now being the most important effect. Again the $6p$ hole is more important in UO_2 than in UO_2^{2+}. The off-diagonal $\langle 5p|6p \rangle$ contributions in $1\pi_u$ and $2\pi_u$ have the signs expected from bonding resp. antibonding orbitals with O $2p_\pi$, but play a much more modest role than in σ_u since they almost cancel each other. In fact, it is slightly artificial to consider $1\pi_u$ and $2\pi_u$ from the point of view of bonding resp. antibonding U $6p_\pi$-O $2p_\pi$ character. These orbitals mix very little in $1\pi_u$ and $2\pi_u$. It is more natural and illuminating to consider the $2\pi_u$ orbital as the f_π-p_π bond which it primarily is ($1\pi_u$ is simply U $6p_\pi$ with very little O $2p_\pi$ admixed; see Table 1). So $2\pi_u$ is just like ϕ_{bond} in Eqs. (6–8), with f_π and p_π being ϕ_A^v and ϕ_B^v respectively. The $6p_\pi$ in this orbital is then simply the highest core orbital, ϕ_A^c in this MO. The term $\langle 6p|6p \rangle$ now represents the diagonal core contribution $c_B^2 a^2 \langle \phi_A^c | h_{\text{MV}} | \phi_A^c \rangle$ of Eq. (8). It is strongly contracting, in agreement with the contracting role we attribute to the core orbital in a simple bonding orbital. Note that this contraction occurs irrespective of the nature of the valence AO, whether contracting such as Au $6s$ in AuH or Au_2 [2] or expanding such as U $5f$ here. There is also a nonnegligible $\langle 5f|5f \rangle$ contribution in $2\pi_u$, corresponding to the diagonal valence term $c_A^2 \langle \phi_A^v | h_{\text{MV}} | \phi_A^v \rangle$. This contribution is much smaller than the core contribution $\langle 6p|6p \rangle$, illustrating the remarks on relative importance of valence and core contributions made earlier. The $\langle 5f|5f \rangle$ contribution is not completely negligible due to the relatively large MV matrix element of the $5f$ (cf. Table 4). The sign of the $\langle 5f|5f \rangle$ contribution depends on the change of c_A with distance. In UO_2^{2+} $5f$ character is lost from $2\pi_u$ upon bond shortening, in UO_2 the $5f$ character slightly increases. These trends agree with the composition of the $2\pi_u$ discussed in Sect. 3 and illustrate that the valence contribution in a simple bonding orbital may, contrary to the core contribution, work in either direction.

Concerning the role of the next deeper core orbital, the U $5p$, we first note that it has a much smaller contracting diagonal contribution than $\langle 6p|6p \rangle$ despite its large MV matrix element. This illustrates numerically that deep core orbitals, even if they may have huge kinetic energy and MV matrix elements, still make smaller contributions to the kinetic repulsion and its MV reduction than the upper core orbital. As a matter of fact, taking also the off-diagonal contributions into account may result in an opposite effect of the next deeper core orbital: since it will have the same phase as the upper core orbital (this phase being determined by the orthogonality condition of ϕ_B^v on the respective core AOs), the off-diagonal contribution between the two core AOs will have opposite sign to the diagonal contributions and may be larger than the diagonal deep core contribution if the off-diagonal MV matrix element is significant. This is clearly demonstrated by the $\langle 5p|6p \rangle$ contribution in $2\pi_u$. Note that the present orthogonality argument for the sign of the $\langle 5p|6p \rangle$ contribution in $2\pi_u$ does not contradict the previous one based on antibonding U $6p_\pi$-O $2p_\pi$ character: the

U 6*p* has opposite phase to the O $2p\pi_u$ combination (and therefore the same phase as U 5*p* in this MO) whether considered as antibonding valence orbital to O $2p\pi_u$ or as mixing into O $2p\pi_u$ for orthogonality reasons. The importance of the upper core orbital that we have pointed out here is of course not contradicted by the fact that the MV matrix elements build up almost completely [35] in the inner core wiggle (2*p* in this case) of the upper core AO. This *does not mean* that the actual innermost core AOs such as 1*s* or 2*p* have any special importance for the relativistic effects on the bond length.

5. Conclusions

The origin of the unusual relativistic expansion of the bond length in UO_2^{2+} and UO_2 has been traced to the special shell structure of the U atom. The presence of the semi-core 6*p* shell in U is the most important single electronic structure feature that leads to the bond lengthening. The 6*p* shows some core character in that it has large MV matrix elements, both diagonal and off-diagonal (with 5*p*). The U 6*p* is not true core in the sense that it is fairly extended, even more so than the valence 5*f*, and is not at very deep energy. The short bonds set up by the 5*f* cause the 6*p* to overlap strongly with the O orbitals and it is sufficiently high in energy that some 6*p* character can appear in the virtual spectrum: there is a 6*p* hole. Bond shortening increases the 6*p* hole, leading to a loss of mass-velocity stabilization. This is the most important cause for a negative slope of $\Delta E^1_{\mathrm{rel}}$.

The second contribution comes from off-diagonal $\langle 5p|h_{\mathrm{MV}}|6p\rangle$ matrix elements, which lead to bond expansion if 6*p* and 5*p* occur in an MO with the same phase. The 5*p* will always have opposite phase to the dominant O AOs because of the core orthogonality condition. There are also occupied orbitals in which the 6*p* has opposite phase to the O AOs, i.e. is antibonding to them, since the 6*p* is sufficiently deep in energy that both bonding and antibonding orbitals are occupied. This situation holds for the $2\sigma_u$ and $3\sigma_u$. In $2\pi_u$ the 6*p* is not the main valence AO on U, but the $5f\pi$ is. The antibonding phase of $6p\pi$ in this orbital with respect to O $2p\pi_u$ combination, which it shares with the $5p\pi$, may be looked upon either as a "core" orthogonality effect, or as antibonding counterpart to the slight in phase mixing between $6p\pi$ and O $2p\pi$ in $1\pi_u$.

In our first order relativistic perturbation approach, relativistic bond length changes are not connected with relativistic changes of the valence AOs. Bonding by a relativistically expanded 5*f* AO, such as in orbital $2\pi_u$ here and in the actinocenes [20], leads to contraction by the MV reduction of the kinetic energy repulsion coming from the core orthogonality condition (the Pauli repulsion), just as in the case of bonding by relativistically contracting *s* valence AOs [2]. In uranyl, however, the main MV effects do not come from the $f\pi$-$p\pi$ bond (orbital $2\pi_u$) but from other orbitals in which the U 6*p* with its special characteristics plays a major, bond expanding, role. The present analysis of the "anomalous" bond lengthening in uranyl thus corroborates the picture of relativistic effects on bond lengths given in Ref. [2].

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