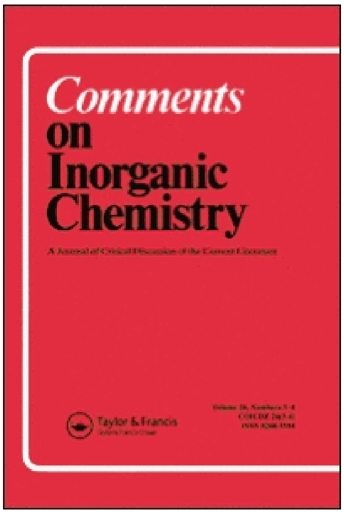

**Comments on Inorganic Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Comment to the Bigeleisen's Theory of Isotope Chemistry of the Heavy Elements

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**To cite this Article** Mioduski, T.(1999) 'Comment to the Bigeleisen's Theory of Isotope Chemistry of the Heavy Elements', Comments on Inorganic Chemistry, 21: 1, 175 — 196
**To link to this Article: DOI:** 10.1080/02603599908020422
**URL:** http://dx.doi.org/10.1080/02603599908020422

# Comment to the Bigeleisen's Theory of Isotope Chemistry of the Heavy Elements

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(Received 15 September, 1998)

The recent Bigeleisen's Theory of isotope chemistry of the heavy elements is discussed in terms of nuclear charge size and shape variations, mass formula, even-odd and odd-odd effects, magic numbers, nuclear field shift versus resulting contraction or expansion of the s, p, d, and f shells, and corresponding variations of the isotope ionic radii and isotope ionization potentials. The effects of even-odd, odd-odd, magic and doubly magic nuclei, as accompanied by a decrease of the nuclear charge size, are of the same sign at the same orbitals of the outermost electrons. Therefore, these effects alter the chemical equilibria of the isotope exchange in the same direction. An expansion of the nuclear charge distribution, usually associated with the addition of neutrons to a nucleus, causes all the s orbitals, and to a lesser extent all the $p_{1/2}$ orbitals, to expand, resulting in a less effective screening of the nucleus. In consequence, the outer d and all the f orbitals become less diffuse, i.e. they contract. The emphasis is given to the uranium isotope chemistry. It is indicated that the uranium ions involved in the Chemex and Asahi technologies must have the outermost electrons on the s or p orbitals in the respective organic or resin phase complexes, and on the f orbitals in the uranium species of the aqueous phase: $U^{3+}$ - $[Rn]5f^3$ versus $U^{4+}$ - $[Rn]6d^1 7s^1 5f^0$ for the Chemex cascade solvent extraction, and $U^{4+}$ - $[Rn]5f^2$ versus $O{\equiv}U{\equiv}O^{2+}$ $-6p^6 \Pi_g^4 \Pi_u^4 \sigma_g^2 \sigma_u^2 5f^0 6d^0 7s^0$ for the Asahi process, where the complexes adsorbed by the anion exchange resin correspond to the organic phase species. We conlude that the isotope ions of the heavy elements that have the outermost electrons on the $d_{5/2}$ or

$f_{7/2}$ and $f_{5/2}$ subshells in the organic phase species and on the s or $p_{1/2}$ orbitals in the aqueous phase complexes should display the inverse chemical isotopic effect in comparison with that reported for the chemical uranium enrichment.

Keywords: *isotope chemistry, chemical uranium enrichment, nuclear charge size of the isotopes versus behavior of the s, p, d, and f electrons*

There are two Bigeleisen's theories of the isotope chemistry for the heavy elements. The first one[1–3] declares that the ln $\alpha$ value, where $\alpha$ is the isotope separation factor, depends on the vibrational quantum effects, and it is proportional to $(M_H-M_L)/M_HM_L \times b/T^2$. In this mass factor M stands for mass of the heavier (H) and lighter (L) isotope, T is absolute temperature and b represents a difference in potential energies and stretching force constants between right hand and left hand side complexes of isotopic exchange equilibria, e.g.:

$$^{235}UA_{aq}+{}^{238}UB_{org} \Longleftrightarrow {}^{238}UA_{aq}+{}^{235}UB_{org} \qquad (1)$$

where the uranium isotopes can be replaced by those of any other heavy element of a lesser importance.

According to this theory[1–3], therefore, differences in chemical behavior, resulting in isotope fractionation, depend on molecular vibrations and stretching force constants in the right hand versus left hand side isotope complexes. This implies[1–3] that the heavier isotope should accumulate in complexes of larger-force constants, i.e. of stronger bondings, which scale for Eq. (1) with the (238-235)/238x235 value, essential for this zero-point energy effect.

The chemical uranium enrichment plant, based on the Chemex[3] cascade solvent extraction, is reported[3] to be generally less expensive, as far as the unit separation costs are concerned, as regards the commonly used physical methods based on gaseous diffusion and gas centrifuge, dealing with $UF_6$. The principal central ions in Eq. (1), of the chemical exchange reaction of the uranium isotopes between different oxidation states, are $U^{3+}_{aq,\ HCl}$ and $U^{4+}_{TBP,\ xylene}$ for the French Chemex process, and $\alpha$ on average is $2.3\times10^{-3}$, whereas the stability constant at 293 K for Eq. (1) is equal to 1.0027. This means that the $^{235}U$ accumulates in the $UCl_4$ adducts with TBP (tri-n-butyl phosphate) of rather stronger bondings and of larger force constants than those in the hydrated complexes of U(III), where the $^{238}U$ fractionates[3]. So, to be extracted, the uranium ions are supposed to be dehydrated, solvated by TBP, associated with the chloride counter-ions by forming the ion-pairs and the respective neutral complex. It is not clear whether the partition of the final complex between the phases is the last step because generally the order of the successive stages remains unknown in such a solvent extraction. (Fortunately, this order is unimportant from the thermodynamic point of view.)

In the respective Japanese Asahi (ACEP)[3] chromatographic pilot plant, the major central ions in Eq. (1) are $UO_{2,\,r}^{2+}$ and $U_{aq}^{4+}$, where r denotes an anion exchange resin. Moreover, the $K^0$ value for Eq. (1) exceeds unity, being equal to 1.0013, and the $^{235}U$ isotope minutely concentrates in the complexes of uranium at the higher oxidation state, adsorbed by the organic resin, with the $\alpha$ value equal[3,8] to $1.3\times10^{-3}$. Therefore, the resin displays a preference for the $^{235}U$ in the anionic chloride complex of U(VI) with regard to the strongly hydrated U(IV) complex.

Thus, both the Chemex and Asahi data[3], of the most significant parameters best statistics possible, are in contradiction with the first Bigeleisenъ Theory [1-3], or at least apparently so. In addition, Fujii et al.[4,5] called attention to the even(Z)-odd(N) chemical effect (the recent term) displayed by the isotopes of $_{92}U$, and of some other metals[6,7]. Fujii et al. erroneously attributed an anomaly for the $^{235}U$ isotope of the odd mass number to the nuclear spin of $^{235}U$. It has been found that the uranium isotopes of the even mass number A: $^{234}U$, $^{236}U$ and $^{238}U$ exactly obey the linear dependence[1-3] on the $\Delta M/M_H \cdot M_L$ factor. Whereas $^{235}U$ is shifted towards the neighboring isotope of the lower mass number, and its chemical behavior corresponds to 234.5 nucleons. In other words, the $\alpha$ value is 1.76 times larger for the $^{235}U/^{238}U$ than for the $^{236}U/^{238}U$ pair and, according to the mass factor, it should be only 1.50 times larger. The Chemex and Asahi uranium enrichment plants, based on classic inorganic technology, probably would not be built as competitive even with the most prospective photochemical laser methods of uranium enrichment of MLIS and AVLIS[8], without unknowing presence of the even-odd effect of the $^{235}_{92}U$ isotope.

After nearly 50 years, when Bigeleisen's Theory, originally published with Maria Goeppert-Mayer[1], was employed[3] in chemical practice, Bigeleisen presented another theory[9] concerning this important area – which is one of the most subtle in coordination chemistry. According to the recent theory, the decisive factor for the chemical enrichment of uranium are the isotopic variations in the nuclear charge size (resulting in the volume isotope effect) and shape (i.e. deformations of the nucleus) that cause the nuclear field shift and affect outer electrons, determining a chemical behavior and photoelectron spectra. The nuclear spin effect of the odd-A-nuclei, producing hyperfine splittings in electronic spectra, has been shown[9] to be ten times too small to explain the even-odd effect in the solution chemistry of the uranium isotopes. So, these are the changes in the nuclear charge surface density with changing neutron number that alter the electron energy levels resulting in the even-odd staggering in optical spectra of uranium and heavy metals such as Hg, Ce and so forth. The odd-neutron isotope level is displaced toward the next lower even isotope, e.g. $^{238}$U-4244.3724Å, $^{236}$U-4244.226Å, $^{235}$U-4244. 1211Å, $^{234}$U-4244.075Å and $^{233}$U-4243.977Å[10]. In case of uranium this staggering in the optical spectra is adequate to explain quantatively the anomalous behavior of the $^{235}$U, and that of the $^{233}$U, i.e. the enhanced $\alpha$ values for the even-odd isotopes. The vibrational energy term has been proven[9] to be about three times smaller and, most importantly, opposite in sign to the nuclear field shift. Thus, it is not the vibrational term, nor the nuclear spin effect nor the specific mass isotope effect either (contrary to the latter effect of the coupling of the motion of the nucleus and the electrons, the normal mass isotope effect of the reduced mass correction is quite negligible for heavy elements; besides the normal mass effect always varies with the mass factor in the same direction as the vibrational term), but the nuclear field shift that determines the direction of the H versus L isotope fractionation. This makes clear the chemical even-odd effect observed as well as the concentration of the heavier isotope, that is the $^{238}$U, in the aqueous phase complexes of uranium at the lower oxidation states, and presumably, on avarage, of weaker uranium bondings and of smaller stretching force constants.

## INFLUENCE OF THE ISOTOPE NUCLEAR CHARGE DISTRIBUTION ON THE s, p, d, AND f ELECTRONS

The nuclear field shift, and its chemical consequences for the isotope chemistry, are due to the change in the electrostatic field of the nucleus, namely to the change in the size and shape of the nuclear charge distribution in the isotopic modifications of the central ions.

The magnitude and direction of the free energy of the nuclear field shift for Eq. (1), $\Delta G_v^0$, depends on the change in the surface charge density of the nucleus, $\delta\rho_{ch}(r)$, which influences directly (s and p orbitals) or indirectly (d and f orbitals) even the outermost electrons. This influence must be related to orbital energies, electronic spectra, ionization potentials, isotopic ionic radii, complexation, solvation, aquation, adsorption, redox and partition properties and so forth and, in consequence, to the minute changes in the isotope distribution in the bi-phase exchange equilibria (1).

According to the Shannon's ionic radii, the ionic radius at the coordination number 6 is equal to 102.5 pm for the $U^{3+}$ ion and to 93 pm for the $U^{4+}$ ion. The difference between the isotope ionic radii for the $^{238/235}U$ pair was rather underestimated[11] to be less than $10^{-4}$ pm.

Usually, the addition of a neutron to a nucleus implies a radial expansion of the nuclear charge. This increase of the volume charge size is accompanied by a radial expansion and a destabilization of the electronic orbital that approaches the nucleus most closely, viz. The 1s orbital, containing the only electrons with a large probability of being at the nucleus. Because the higher s shells must be orthogonal versus the lower ones, all the s atomic orbitals must reveal a similar destabilization and a spacial expansion. Like the 1s orbital, they are getting further from the nucleus and their <r>-expectation values are becoming larger by a direct expansion. Due to the interacting expansion of the nuclear charge size of the heavier isotope, and the electronic shell structure effects, the expansion and destabilization of the outermost s shell, e.g. of the 7s shell of uranium, can, in fact, be even larger than that of the respective 1s shell.

The mechanism of this phenomenon must be similar, but of the opposite direction (in case of the increasing nuclear charge size), as for the superimposed relativistic (spin-orbit) effects[12–14]. The latters result from relativistic speeds of electrons in the near vicinity of a nucleus which speeds grow roughly like $Z^2$. In consequence, these relativistic speed electrons are getting distinctly more mass, and are getting closer to the nucleus.

For the s electrons, with no orbital angular momentum, l=0. In the case of l>0, i.e. for the p, d, and f electrons, the relativistic spin splitting occurs into the vector sum, **j=l+s** ; j=l±1/2. For the p electrons of l=1 this splitting has two j values, j=1/2 and j=3/2, subscripted as $p_{1/2}$ and $p_{3/2}$. As a result, all the $p_{1/2}$ electronic orbitals and at least all the inner $p_{3/2}$ subshells, which exhibit also the finite electron density at the nucleus, increase their radial extension into all the shells with increasing nuclear charge size. Only the s electrons, and, to a much lesser extent, the p electrons come into and probe the nucleus "feeling" directly its size and shape related to the neutron number, the pairing energy, nuclear shell effects et cetera. It results from the present paper that even the outermost $p_{3/2}$ electrons[12] do not show a definite opposite trend with the increasing nuclear charge radius, and presumably they remain unchanged or slightly expand. It is assumed that for the s and $p_{1/2}$ electronic orbitals, their respective probability wave function has approximately constant and different from zero value in the nuclear volume, $|\Psi(0)|^2 \neq 0$. This value varies with r starting from the surface of the nucleus. In case of uranium, we extrapolate the density of the $p_{1/2}$ electrons at the nucleus to be about 15% of that for the s electrons. This estimation is based on the squares ratio of the probability wave functions, $|\Psi(0)|^2(np_{1/2})/|\Psi(0)^2(ns)|$, which increases with Z and was reported[15] to be 0.101 for $_{79}$Au, and 0.128 for $_{87}$Fr. The usual expansion of the nuclear charge distribution for the heavier isotope, followed by the respective expansion of the s and p orbitals, is the reason why the s and p orbiting electrons screen the nuclear attraction less efficiently. Therefore, due too a minutely stronger attraction by the nuclear protons, at least the $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$ orbitals must be shortened radially and indirectly stabilized, i.e. they exhibit lowered energies. So, the radial size of the d and f orbitals changes inversely to the radial size of the nuclear charge and inversely to the <r>-expectation values of the s and p electronic orbitals. It is the change in the electron density at the nucleus, $\Delta(\Psi(0)^2$, when neutrons are added, that counts. The screening of the nuclear charge is the most effective by the 1s, and to a much lesser extent, by the 2s and $2p_{1/2}$ electrons. (The differentiation of the s and p electrons as e.g. 1s, 2s versus 7s or $2p_{1/2}$ versus $6p_{1/2}$ electrons has a rather visual than physical meaning. The valence s and p electrons also probe the nucleus and have relativistic speeds in the vicinity of the nucleus by their orthogonality. They also get closer to the nucleus due to the relativistic effect, and get further from the nucleus if the nuclear charge radius increases, as e.g. from $^{235}U$ to $^{238}U$, being affected in a similar way as the innermost s and p electrons). The d and f electrons practically never come in the direct vicinity of the nucleus due to their high angular momenta and the centrifugal energy[12], which scales with $l(l+1)/r^2$. The outer d and all the f shells have no inner ones against which they would have to be orthogonal, i.e. they "feel" no original repulsion[12]. Therefore, it is possible that this indirect effect of the isotope electron stabilization and orbital contraction — e.g. in case of all the 5f orbitals, and especially of the $5f_{7/2}$ and $5f_{5/2}$ subshells of the $^{238}U$ — make these isotopic orbitals less accessible for chemical bondings[16] than in the case of the respective $^{235}U$ complexes described by Eq. (1).

In other words, an increase of the nuclear charge radius implies a decrease of the ionization potential (IP) of the s and $p_{1/2}$ electrons, and the net reversed effect, i.e. an increase of the IP, for the outer d- and of all the f electrons. The location of the outermost electrons of the central ions in both phases, i.e. whether they are on the s and p or d and f orbitals, must also be reflected by respective minute differences between isotopes of the heavy elements. These differences concern isotope ionic radii[11], and consequently complexation and redox properties (the latters depend on ionization potentials and complexation, aquation, solvation, adsorption, and possibly association of the central ions in both phases and in both oxidation states), and the partition stage as well. The partition constants of the final complex between two immiscible phases, next to the stability constants of the widely understood complex formation, determine the values of the extraction coefficients or distribution ratios and the resulting effectiveness of chemical isotope separations.

## CHEMISTRY OF THE URANIUM ISOTOPIC EXCHANGE EQUILIBRIA

Generally, the nuclear field shift is a differential effect that operates according to the changes in the nuclear charge distribution of the central isotope ions between the right hand versus left hand side equilibrium complexes. In the case of the isotopic exchange equilibrium (1), employed for the enhanced $^{235}U$ separation in the redox reactions, the molar free energy of the nuclear charge volume or field shift can be given as:

$$\Delta G_v^o = -RT \ln K_v = +RT \left\{ \left[ \ln({}^{238}UB_{org})_v - \ln({}^{238}UA_{aq})_v \right] - \left[ \ln({}^{235}UB_{org})_v - \ln({}^{235}UA_{aq})_v \right] \right\} \quad (2)$$

$$= +RT \left\{ \left[ \ln({}^{238}UB_{org})_v - \ln({}^{235}UB_{org})_v \right] - \left[ \ln({}^{238}UA_{aq})_v - \ln({}^{235}UA_{aq})_v \right] \right\}$$

where the logarithms of the thermodynamic activities of the equilibrium exchange (1) of the uranium isotope species cover only the nuclear field shift (i.e. in practice the volume charge shift with a subscript v). Therefore, the $\Delta G_v^o$ value, expressed by Eq.(2), is by about 30% more negative than the net $\Delta G^0$ value. It is because the net Gibbs energy for Eq. (1) covers also the vibrational term of the opposite sign[9] and all the other terms, estimated[9] to be virtually negligible. The negative, i.e. exothermic, value of the $\Delta G^0$ for Eq. (1) is the experimental fact established in both the Chemex and Asahi plants[3,8,9]. The more negative Gibbs energy of the volume shift given by Eq.(2), the more negative the net $\Delta G^0$ value, and the higher concentration of the $^{235}U$ isotope in the organic or resin phase complexes of uranium at the higher oxidation state.

In Eq. (1) the major species are supposedly as follows[3,8]:

Chemex: U(IV) complex, $UCl_4 \cdot 3TBP_{org}$, versus U(III) complex, $[ClU(OH_2)_7]^{2+}_{aq}$ , In the latter complex, the original uranium coordination number (CN) in the $[U(OH_2)_9]^{3+}_{aq}$ aquo ion[18] is probably decreased by the presence of the $Cl^-$ ion. Thus, the uranium ions are extracted as neutral and presumably anhydrous adducts, trisolvated by tri-n-butyl phosphate (TBP).

Asahi: U(VI) complex, $(UO_2Cl_4)^{2-}_r$ (a decreased CN in comparison with that in the aquo ion, $[(H_2O)_5(UO_2)]^{2+}_{aq}$ , and probably the same as in the consecutive chloride complexes, $UO_2Cl^+_{aq}$, $UO_2Cl_{2,\ aq}$, $UO_2CL^-_{3,\ aq}$, which also occur in the aqueous phase of about 4M $HCl_{aq}$) versus U(IV) complex, $[ClU(OH_2)_6]^{3+}_{aq}$ (a decreased CN in comparison with the original CN[3,8] in the aquo ion, $[U(OH_2)_8]^{4+}_{aq}$ ). In this case, an adsorption of the bi-negatively charged uranium complex on a resin anion exchanger is employed.

Although in solution complexes, especially in dilute solutions, the CN always remains controversial, it is certain that uranium at the higher oxidation state in the organic or resin phase complexes, $UB_{org}$, has a lower CN than in the $UA_{aq}$ species of Eqs. (1,2).

The electronic ground state configurations usually are given as:

$$U^{o} - [Rn]\,5f^{3}6d^{1}7s^{2}; \quad U\,(III) - [Rn]\,5f^{3}; \quad U\,(IV) - [Rn]\,5f^{2};$$
$$U\,(VI) - [Xe]\,4f^{14}5d^{10}6s^{2}6p^{6};$$
$$O \equiv U \equiv O^{2+} - 6p^{6}\Pi_{g}^{4}\Pi_{u}^{4}\sigma_{g}^{2}\sigma_{u}^{2}5f^{0}6d^{0}7s^{0}\ ^{12-14}$$

The equatorially coordinating and linear uranyl with triple bonds is the 6p ion and the $6p\langle r^{-3}\rangle$ integral is much larger than the respective 6d or 5f integrals (i.e. 80.61, 4.52 and 5.71 for the $6p_{3/2}$, $6d_{3/2}$ and $5f_{5/2}$ subshells, respectively, and therefore the major contribution to the nuclear quadrupole coupling constant of the $^{234}UO_2{}^{2+}$ ion originates in the 6p electrons[14]).

The relativistic effects narrow the ranges of orbital energies, i.e. they decrease the differences in the radial extension (expectation root mean square radius, $\langle r^2\rangle^{1/2}$, or simply $\langle r\rangle$-expectation value) of the 5f, 6d and 7s orbitals of uranium[12,13,16]. They make the 7s orbital of all the uranium isotopes more compact, of a lower energy, and the 7s electrons stronger bound by a direct relativistic orbital contraction. Due to a relativistically increased screening of the nucleus by the contracted s and p electrons, the 5f orbitals, by a sort of a mirror image, become larger, of a higher energy, and more loosely bound in result of this indirect relativistic orbital expansion[12].

It should be noted that the Chemex results[3] reported of the uranium enrichment cannot be explained by the favored solvent extraction of the $^{235}UB_{org}$ species from Eqs. (1,2) when the ground state electronic configuration of the $U^{4+}$ ion, specified above, is valid for the U(IV) adducts of TBP. The ground state configuration would rather result in positive $\Delta G_{v}^{o}$ values for Eq.(2). However, because the energy levels of the 5f, 6d, 7s, and 7p uranium orbitals are close each other, and the differences in energy between them are of the order of the chemical bonding energy, the electronic configurations of uranium at a definite oxidation state and for a definite complex can differ depending upon ligand surroundings[16].

Provided the solvent extraction and the anion exchange favor the fractionation of the $^{235}U_{org}$ (in the prevailing complexation/ligation term but not in the smaller and opposite partition term) the electronic configurations of the uranium ions involved in Eq. (1), are expected to be as follows:

$U^{3+}$ – $[Rn]5f^3$ versus U(IV) – $[Rn]6d^1 7s^1$ (or $[Rn]7s^2$) for the Chemex process, and $U^{4+}$ – $[Rn]5f^2$ versus U(VI) – $[Xe]4f^{14}5d^{10}6s^2 6p^6$ for the Asahi process.

The postulated difference in the electronic configurations of the U(IV) between the Asahi ground state configuration, $5f^2$, for $[ClU(OH_2)_6]^{3+}_{aq}$, and the Chemex configuration, $6d^1 7s^1$ or $7s^2$, eventually modified by using the MO convention, may result from the different lowest energy levels in the anhydrous adducts, $UCl_4$ . 3TBP, extracted by the 35–45% TBP solution in xylene[3] in case of the Chemex technology.

The specified uranium ion electronic configurations, with the outermost electrons on the s or p orbitals at the higher oxidation state, favor the fractionation of the $^{235}U$ by the extractant or the anion exchanger. In turn, the outermost electrons on the f orbitals at the lower oxidation state of uranium support additionally the accumulation of the $^{235}U$ in the organic or resin phase by favoring concentration of the $^{238}U$ species in the aqueous phase due to a smaller radial extension of the outermost f electrons for the heavier isotope and a resulting stronger hydration of the $^{238}U$ ions. (In the organic or resin phase, on the contrary, the radial extension of the outermost electrons should be smaller for the L-isotope ion and, in consequence, the complexation term (all sorts of ligation in the non-aqueous phase included) is expected to be larger, i.e. of more negative Gibbs energy for the L-isotope than for the H-isotope species). In the bi-phase equilibria the partition term usually counteracts to the complexation term (aquation, solvation, association and adsorption by the resin included) due to the entropic factor. This means that larger molecules of the final complex, which are less strongly hydrated in the second coordination sphere, are more readily "pushed out" from the aqueous phase stretched by the hydrogen bondings than the complex molecules of smaller central isotope ion radii, and consequently of larger complexation (aquation, solvation, adsorption and possibly association included) constants.

The dioxo-uranium ion, $UO_2^{2+}$ , as specified above in the MO convention, has the outer, formally closed 6p shell and the unoccupied; $5f^0$, $6d^0$, $7s^0$ and $7p^0$ shells of decreasing, but close-to-each-other, binding energies. A substantial hybridization of the ligand orbitals with the 6p orbitals of uranium was observed[12–14]. The variations of the <r>-expectation values for the 6p orbitals follow the nuclear charge size variations with a neutron number to a much lesser extent than in case of the respective 7s orbital. This orbital property may elucidate why the Asahi procedure, which employs isotope separation in the U(VI)/U(IV) redox system (where the difference between the oxidation states is two, while it is one for Chemex), and which makes use of the 6p uranyl ion, yields lower unit separation factor (and a lower $K^0$ value for Eq. (1)) than in case of the Chemex U(IV)/U(III) separation[3]. The latter technology presumably takes advantage of the radial expansion of the most sensitive outermost s electrons of the $^{238}U^{4+}$ ions in the organic phase complex and of the radial contraction of the outermost f electrons of the $^{238}U^{3+}$ ions and their stronger hydration in the aqueous phase. This leads to the enhanced fractionation of the lighter uranium isotope in the organic phase.

Generally, the 5f orbitals have larger radial extensions in comparison with the 7s and 7p orbitals, as it results from considerable overlaps of the 5f orbitals, even with orbitals of the hard O, N, and F donor atoms of various ligands. The 5f actinide orbitals, mostly due to the larger relativistic effects, are more accessible for bonding than the 4f lanthanide orbitals. The resulting differences in the f-electrons covalent contribution to bonding energies are the main reason for the more distinct double-double (tetrad) effect in the actinide than in the lanthanide series[18,19].

Thus, the specified electronic configurations of uranium, with the outermost s or p electrons for all the $UB_{org}$ species, and the outermost f electrons for all the $UA_{aq}$ species in Eqs.(1,2), are in accord with the observed concentration of the $^{235}U$ isotope in the $UB_{org}$ species of Eqs. (1,2). This conclusion is based on the behavior of the s, p, d, and f electrons that is affected by both the relativistic (spin-orbit) effects[12] and ligand surroundings (as far as which orbital, s, p, d, or f, is the outermost for the central ion in a given complex) and by the superimposed nuclear field shift that minutely differentiates (in energy and consequently in the number of molecules which, according to the mass action law, constitute the thermodynamic activities in Eqs. (1,2)) the $^{235}U$ isotope species from the respective $U^{238}$ species of the same stoichiometry.

When analysing the complexation/aquation/solvation/adsorption terms versus partition terms referred to by Eq. (1,2), the difference in the ionic potential, as the major factor for the respective $\Delta G^o_v$ values, (+4/r($U^{4+}$) versus +3/r($U^{3+}$), and +6/r(U(VI) versus +4/r($U^{4+}$) between $^{235}U$ and $^{238}U$ should be taken into account. Generally, the ionic radius and the coordination number (CN) of uranium is smaller in the organic or resin phase than in the aqueous phase[18]. It is likely, as suggested above, that CN is 7 versus 8 for the Chemex, and 6 versus 7 for the Asahi process, respectively. This makes the bondings shorter, the stretching force constants larger, and the respective electronic energy levels of uranium ions more stable i.e. lower[9] in the organic or resin phase and for the $^{235}UB_{org}$ than for the $^{238}UB_{org}$species of Eq (1). The isotope separation is the most effective for a stronger interaction of the $^{235}U$ ions of the smaller <r>-expectation value of the outermost s or p orbitals in the $UB_{org}$ species, and a weaker interaction due to the outermost f electrons in the $UA_{aq}$ complexes, when compared with the respective $^{238}U$ complexes.

The main contribution in bondings of the species given by Eqs. (1,2) is the ionic contribution and electrostatic interactions, discussed in terms of the charge/radius ratio of the central ion and the CN – ionic radius interrelation. (Similarly as the $\Delta G^o_v$ for Eq.(2) is the decisive component of the net $\Delta G^0$ value for Eq. (1)). There is no foundation to consider the electrostatic contribution to be smaller, in proportion to the total bonding energy, for the isotopic exchange (1) than for regular ionic chemical equilibria where differences in neutron numbers of the central ions are neglected.

Therefore, to be explicite, it should be added in proof that if the nuclear charge size of the $^{235}U$ is smaller than that of the $^{238}U$, which is certain, then the isotope ionic radius of the extracted $^{235}U^{4+}$ ion must be smaller than that of $^{238}U^{4+}$ in the Chemex process, provided the outermost orbital of the $U^{4+}_{org}$ ion is the 7s orbital. In the case of the 5f outermost electrons, the isotope ionic radius of the $^{235}U^{4+}$ ion indisputably would be larger than the respective value for the isotope ions of $^{238}U^{4+}$ Thus, the accumulation of the $^{235}U^{4+}$ ions in the organic phase in the Chemex process gives an indication that the U(IV) has 7s outermost electrons in the extracted species. Otherwise, in case of the presence of the 5f electrons, which change their radial extension inversely to the nuclear charge size, it would be the aqueous phase which is expected to get richer in the $^{235}U$ isotope. It is assumed that the complexation term (aquation, solvation, association, adsorption – by anion – exchanger included) prevails over the partition term in the bi-phase equilibria. Both terms are $r_U$-dependent and, as mentioned above, they display the opposite directions. It is impossible that the central ion-ligand interactions increase with the charge/radius ratio more rapidly in the aqueous phase than in the organic phase and that the free energy of the Chemex extraction becomes more negative with increasing isotope ionic radius. Such an exceptional case is possible only if the central ions are in the same oxidation state as for the unique Ln(III) solvent extraction system employed for some studies on the double-double effect[18,19]. This exceptional case presumably results from an extra stronger hydration of the heavy lanthanides(III) in their aquo ions that contain not 9 but 8 water molecules[18].

Unfortunately, a precise quantitative discussion, beyond that given by Bigeleisen[9], is not possible at present for such an extremely minute, and differential in nature, chemical isotopic effect as that discussed in this paper. Therefore, the effect is discussed merely in the "larger-smaller" categories.

It results from this discussion and qualitative estimations that both expressions of Eq.(2) (i.e. this balancing the differences in logarithms of the thermodynamic isotope activities, between the same isotope in different phases and oxidation states, and this comparing the differences in logarithms of the equilibrium activities of isotopic exchange (1) between the heavier and the lighter isotope in the same phase and oxidation state) are the most negative, and the $\Delta G_v^o$ value is the most exothermic, provided the $5f^3(U^{3+})$ versus $7s^{1 or 2}$ $(U^{4+})$ and $5f^2$ versus $6p^6(UO_2^{2+})$ are the outermost orbitals of the isotope central ions in Eqs. (1,2).

Clearly, the negative value of $\Delta G_v^o$ in Eq. (2) arises from the fact that the $^{235}U$ (smaller nucleus) cations, generally, are of smaller radial electron extension, i.e. they are energetically stabilized, with respect to the $^{238}U$ (larger nucleus) cations of the higher level of the electronic energy in the organic or resin phase species, and *vice versa* in the complexes of the aqueous phase.

Except the Gibbs energy of complexation of the central ions in the both oxidation states (i.e. aquation, solvation, association and adsorption by the resin included), the isotope redox effect for Eqs. (1,2) is dependent on differences in ionization potentials (IP) of the isotopic central ions. The IP of the $^{235}$U ions with the 5f outermost electrons in the $^{235}UA_{aq}$ species must be lower than the IP for the respective $^{238}$U ion. (The 5f orbitals contract with the increasing nuclear charge size). This is expected to cause a raise of the $^{235}$UA/$^{238}$UA ratio at the higher oxidation state of uranium. It appears, however, that the IP factor is insufficient to prevail over the possible opposite effect of the decisive total complexation term (the latter is diminished by the opposite bi-phase partition term) for the respective species of Eq. (1). To make the isotope separation the most effective, the IP value and the free energy of solvent extraction (Chemex) or of anion exchange (Asahi) should act in the same direction. Some suggestions[3] on the decisive role of the redox properties for the isotopic exchange equilibrium (1) are inconclusive.

Summarizing, to maintain that the outer electrons become less tightly bound, of a smaller ionization energy, and that the ionic radius of an isotope always minutely increases with increasing charge size of the nucleus, is not exact. In every particular case, changes in location of the outer electrons, depending on whether they are on the s and p or on the d and f orbitals in the complexes of isotopic exchange equilibria of the Eq. (1) type, must be taken into account. Moreover, as results from the discussion to follow, the nuclear charge distribution is far from smoothly increasing with the number of neutrons N. The addition of a neutron to a nucleus leads to a rearrangement of the entire nucleus, which dosent necessarily mean an increase of the nuclear charge size.

## NUCLEAR SIZE AND SHAPE OF THE ISOTOPES OF THE HEAVY ELEMENTS

The size and shape of a nuclear charge is represented by a probability wave function of the outermost valence protons that has a somewhat less diffused surface than for the outermost electron clouds in atoms[17]. The halfway charge radius of a nucleus, $R_{ch}$, for which a nuclear charge density decreases by 50%, depends mostly on a number of nucleons A. As a crude estimate, in approximation of a Fermi uniform spherical charge distribution, it is often given by a simple formula:

$$R_{ch} = r_o A^{1/3}, \text{ where } r_o \text{ is } 1.1 \div 1.3 \text{ fm } \left(1 \text{ fm} = 10^{-15} \text{m}\right) \qquad (3)$$

However, in a nucleus the proton distribution is not quite uniform. Besides, it lies within the neutron distribution. For instance, in case of the doubly magic $^{208}$Pb, the root mean square radius for the proton sphere $< r_p^2 >^{1/2}$ is about 5.4 fm, and it is about 5.6 fm for the neutron sphere[17]. This results from both the Hartree-Fock calculations and the scattering data for electrons or muons (electromagnetic interactions reveal the protons distribution), and for neutrons or α-particles (strong nuclear interactions supply neutrons and nuclear matter distribution data). So, the $R_{ch}$ value, which differs from the nuclear protons radius[17], changes slower than $A^{1/3}$, and slower than the radius of the neutron distribution when neutrons are added. This gives rise to "a neutron skin". For a given heavy nucleus the mean square nuclear radii decrease, corresponding to the respective probability wave functions of the outermost nucleons, $|\Psi(r)|^2$, as follows: $< r_n^2 > \, > \, < r_m^2 > \, > \, < r_p^2 >$ (where subscripts denote, respectively, n-neutron, m-matter, as an average between the respective neutron and proton values, and p-proton).

It is worthy to note that the nuclear shell effects are difficult to predict, and therefore the $< r_p^2 >^{1/2}$ value decreases between the doubly magic $^{40}_{20}$Ca and the doubly magic $^{48}_{20}$Ca from 3.39 to 3.38 fm[20] in spite of eight neutrons added. (For $^{44}$Ca the $< r_p^2 >^{1/2}$ value is 3.42 fm[20]). Obviously, at the virtually constant volume of the $^{40-48}$Ca nuclei, no nuclear field shift, even-odd effect, or the effect of doubly magic nuclei can be observed. The vibrational and the mass isotope effects (it is assumed that the normal isotope mass shift becomes negligible not till than for $Z>40$), scaling with the mass factor in a regular manner can be expected. Besides, as results from the discussion below, the effect of magic nuclei tends to eliminate the even-odd staggering.

To obtain a model of a somewhat "hairy" nuclear charge distribution corresponding to the half-density radius, $R_{ch}$, one can substitute $A=N+Z$ in Eq.(3) by the isotope mass M in the unified atomic mass units, directly related to the nuclear binding energy, B, to the volume, V, and to the shape, S, of the nucleus since these quantities are strictly connected, and a roughly linear relationship is being held, viz. $R_{ch} \propto V_{ch}^{1/3} \propto A^{1/3} \propto M(N, Z, B, S)^{1/3}$. It suffices, then, to use the semi-empirical mass formula[21], and to replace A by M(N,Z,S) in Eq. (3):

$$M(N,Z,S) = 1/c^2 E(N,Z,S) = Nm_n + Zm_p - 1/c^2 B(N,Z,S) \quad (4)$$

The B value in Eq. (4) is given in the below Eq. (5):

$$B = b_{vol}\, A - b_{surf}\, A^{2/3} - 1/2 b_{asym}\, (N - Z)^2 / A$$
$$- 3Z^2 e^2 / 5R_{ch} + \delta B + S\, e^{-(\delta R)^2/a^2}$$

It visibly results from Eq.(5) that, by the liquid drop macroscopic model, the B and, consequently, the $R_{ch}$ values are related to the volume energy, the surface energy, the asymmetry energy of the excess neutrons, N-Z (i.e. the neutrons out of the α-particle structure which structure acts on the charge distribution especially at $A \leq 24$, implying a saw tooth B variation for A=4n where n = 1,2,3...), the electrostatic energy of repulsion of protons in a nucleus, and the pairing energy correction , δB. The δB value amounts to Δ (around $11.46/A^{1/2}$ MeV) for even Z and N, zero for odd A, and -Δ+20/A for odd Z and N. For the odd-odd nuclei a rest interaction of about 20/A MeV between unpaired neutron and unpaired proton occurs. The last term of Eq. (5) represents a shell microstructure correction[22,23] to the Fermi distribution where this correction for heavy elements is equal to less than 1% of the B value. The shell effect amounts to about 3 meV for the magic numbers N=82 or 126. Evidences for the semi-magic numbers of 58, 64 and 96 are inconclusive. For the heaviest nuclei, the magic numbers 108 and 114 are expected for protons, whereas 162 and 184 for neutrons, of which doubly magic nucleus of Z=108 and N=162 is evaluated to be deformed[23]. The last term in Eq. (5), reflecting the shell discontinuity of the B value, and consequently of the $R_{ch}$ value, tends to disappear for aspherical nuclei due to the attenuating factor with increasing δR, i.e. with distortion of the nucleus. Thus, the shell correction in Eq.(5) represents negative dips at the magic Z and N numbers (for a spherical shape $(\delta R)^2=0$, β=0, and a correction is the negative S value), and positive bumps in between when the S function becomes positive[22]. So, the S value changes from an extreme in negative values at the magic numbers to positive values in between. It is proportional to δR, and consequently to the β-parameters, and to the nuclear electric quadrupole moment $Q_2$ that is equal to zero for a spherical charge distribution, and that is small for compact nuclei. A quadrupole deformation reaches minimum for either

Z or N magic numbers[17] which gives evidence that the proton distribution is strictly related to the neutron distribution, and to the neutron magic numbers.

## IS THERE POSSIBLE A CHEMICAL ISOTOPE EFFECT OPPOSITE TO THE EVEN-ODD EFFECT?

It clearly results from Eq.(5) that both the volume and the deformation of the nucleus, and consequently the $R_{ch}$ value, decrease at the magic numbers due to a minimum in the S value. The $R_{ch}$ value decreases also, in reference to the most abundant even-even nuclei, for the odd-odd nuclei by the value corresponding to the $-2\Delta+20/A$ energy, and to the $-\Delta$ correction, viz. to a nearly twice smaller extent, for the odd-A-nuclei which usually display the even-odd staggering. This means that, as results from Eq. (5), all the three nuclear effects, which alter the chemical equilibria of the isotopes of the heavy elements, i.e. the even-odd effect, the effect of a shell closure at the magic N and Z numbers, and the effect of the exceptional odd-odd nuclei, act in the same direction because they are accompanying by a decreased nucleus. (e. g. the even-odd $^{235}_{92}U$ isotope, as far as the nuclear charge size and the chemical behavior is concerned, falls in with $^{234.5}U$). Hence, rather against a chemical intuition, the effect of magic and doubly magic nuclei is not opposite to the odd-A effect but, as acting in the same direction of the decreased nuclear size, it decreases the even-odd irregularity, e.g. for N= 82–1 or 126–1, or it is stronger and tends to eliminate the even-odd staggering for N=82+1 or 126+1.

Therefore, as far as the direct changes in the nuclear charge dimensions are concerned, the inverse chemical effect to the even-odd effect presumably is not possible, at the same configuration of the outermost electrons, either for the odd-odd or for the magic and doubly magic nuclei. However, such an effect is expected to exist, as mentioned above, at the changed orbitals of the outermost electrons. It would be most distinct if the outermost electrons of the central isotopic ions in the organic or resin phase complexes were not the s or p orbital electrons but the $f_{7/2}$, $f_{5/2}$ or $d_{5/2}$ subshell electrons (possibly also the $d_{3/2}$ electrons but not the $p_{3/2}$ electrons) and *vice versa* in the aqueous phase complexes.

## ODD-ODD EFFECT AND THE STAGGERING FACTOR VARIATIONS

The expected odd-odd effect, resulting from Eq. (5), would be smaller in regard to the odd-even nuclei, in comparison with the even-odd effect in regard to the even-even nuclei revealed by Fujii[4,5], and explained correctly by Bigeleisen[9]. On average, it is supposed to be smaller in proportion to the rest pairing energy of unpaired neutron and unpaired proton equal to about 20/A MeV. The odd-odd staggering would consist in the nuclear field shift, accompanied by the addition of one neutron to the odd(Z)-even(N) nuclei that must be less than half that expected due to addition of two neutrons. The staggering factor, $\sigma$, is a function of the changes in the mean square nuclear charge radii, $\delta\langle r^2\rangle$, (where $\langle r^2\rangle$ stands for $< r_p^2 >$ ), which can be split into volume and shape components. By definition $\sigma$ is:

$$\sigma \equiv 2(< r_{A+1}^2 > - < r_A^2 >)/(< r_{A+2}^2 > - < r_A^2 >) \qquad (6)$$

Unfortunately, it is rather difficult to study directly the undiscovered odd-odd staggering, with respect to the odd-even nuclei, in terms of the definition (6) for the rare odd-odd nuclids, which are semistable only thanks to their extra large spin. The odd-odd nuclei have a single stable counter-isotope, i.e. $^{138}_{57}La_{81}$ (0.0902%, $t_{1/2}=1.06\times10^{11}$y) versus $^{139}$La, $^{176}_{71}Lu_{105}$ (2.59(2)%; $t_{1/2}=3.8\times10^{10}$y) versus $^{175}$Lu, $^{180}_{73}Ta_{108}$ (0.01212%; $t_{1/2}>1.2\times10^{15}$y) versus $^{181}$Ta. (For $^{50}_{23}V_{27}$ the nuclear field isotope shift and the resulting odd-odd effect are probably too small to be separated from the normal, specific, and vibrational mass isotope effects. ) Nevertheless, at least some comparisons with neighboring nuclei of Z+1 and Z-1, for which A+2 stable isotopes from Eq. (6) are available, can be made.

Usually, the $\sigma$ value is lower than unity. It is worthwile to note that for the Ba and Tl isotopes, the radii of the odd mass nuclei were even found to be smaller than the radii of the respective nuclei with one less neutron[24,25], resulting in negative $\sigma$ values defined by Eq. (6). In some cases the staggering factor is 0, or it may be even slightly larger than unity. The latter case is supposed to occur therefore, for substantial discontuities at elongated shape nuclei of N= 51, 83 and 127, as a result of a relatively loosely – bound extra neutron (a large $\delta < r_p^2 >$ ), when compared with particularly – compact nuclei and relatively small values of the $< r_p^2 >$ at the magic numbers N= 50, 82 and 126. (This recalls a behavior of the outermost electrons of the noble gases with Z protons and closed electron shells versus those of the respective, Z+1, alkali metals, as far as the first ionization potentials are concerned). Such a situation probably takes place for the A+1 nuclid of the N-magic nuclei, e.g. for $^{142}_{60}\mathrm{Nd}_{82}$ versus $^{143}_{60}\mathrm{Nd}_{83}$.

A distinct discontinuity in the trend of the $\delta < r_p^2 >$ values was revealed on both sides of the doubly magic $^{208}$Pb. As expected, this revealed on both sides of the doubly magic $^{208}$Pb. As expected, this discontinuity, and the respective nuclear field shift, are much larger for isotopes heavier than $^{208}$Pb because the shape of nuclei of the lighter isotopes is close to the spherical shape of the doubly closed shell (i.e. from $^{198}$Pb to $^{208}$Pb, $\delta < r_p^2 >$ is 0.11 fm$^2$ for $\delta$N=2, and from $^{208}$Pb to $^{212}$Pb it is, respectively, 0.20 fm$^2$ [26]). So, the $< r_p^2 >$ value increases more rapidly when neutrons start filling a new shell (unless the outermost unpaired proton is in an s-state, its charge distribution will not be spherical) than when the shell is nearly closed. In Pb the isotope shift for the pair N=128/126 is almost twice as large as that for the pair N=126/124 [27].

The largest $\delta < r_p^2 >$ value was found for the odd-even $^{153,151}_{63}\mathrm{Eu}$ nuclids of an entirely different ellipticity, where the quadrupole moment ratio of the isotopes was reported to be more than two. (For a similar reason, a large isotope shift was reported for the even-even nuclei of the pair $^{150,152}_{62}\mathrm{Sm}$ ).

The chemical exchange isotope effect accompanying the cascade solvent extraction in the $^{153,151}\mathrm{Eu}^{3+}_{\mathrm{HDEHP}} - \mathrm{Eu}^{2+}_{\mathrm{aq}}$ system was studied in this laboratory[28,8]. We established, as in case of the uranium enrichment described above, that the lighter europium isotope fractionates in the organic phase complexes of the higher oxidation state. (Vide the reverse definition of the unit separation factor, L versus H instead of H versus L, employed[28]). This experimental fact can be explained by the electronic configuration of the lanthanide ions, which is characterized by the external octet $5s^2 5p^6$ (E.g. $4f^6 5s^2 5p^6$ for Eu$^{3+}$ versus $4f^7 5s^2 5p^6$ for Eu$^{2+}$). The p outermost shell, which is less sensitive than the s one to the nuclear charge size variations, as in case of the uranyl ion, makes it clear why the unit isotope separation factor is very close to unity in this case and it is easily affected by ligand surroundings[28]. Moreover, for lanthanides, which begin a series of the heavy elements, the specific mass isotope shifts of the electronic-nuclear correlation of either plus or minus energy sign, and especially the vibrational energy terms of the opposite direction, in regard to the nuclear field isotope shift, cannot be entirely neglected.

The decreased charge size of the even-odd nuclei with regard to the respective interpolation for the most abundant even-even nuclei – which corresponds to the $-\Delta$ value of the pairing energy correction, and that is almost twice as pronounced for the odd-odd nuclei – is explained[17] by a tendency of the unpaired nucleon to occupy a lower angular momentum state than the pair of nucleons does. Because the higher angular momentum states display a larger radial extension, in such a state the paired neutron tends to move the protons further out of the center of the nucleus. Clearly, a pair of neutrons, or a pair of protons, occupy a larger space in a nucleus than twice that occupied by unpaired neutron or unpaired proton. It is because a pair, which occupies one nuclear orbital, tends to keep each of its two constituents of the opposite spin (two protons or two neutrons) as far as possible on a nuclear orbital. The deformed nuclei of the odd mass number are reported to be less deformed than the adjacent even ones, and therefore of a smaller nuclear charge size[26]. So, a blocking of a pair of states and lowering the mean square deformation $<\beta^2>$ by the odd nucleon also participate in the decrease of the $R_{ch}$ value for the even-odd and odd-odd nuclei. This mechanism elucidates the enhanced separation factor for the $^{235}U$ and $^{233}U$ isotopes of the odd mass number.

## NUCLEAR CHARGE DISTRIBUTION OF $^{235}$U AND $^{238}$U

Generally, the deformation parameter is $\beta_\lambda$ where $\lambda$=2,4,6... For $\lambda$=2, i.e. for a quadrupole deformation, $\beta_2 = (c - a)/R^o_{ch}$ ; $R^o_{ch} \cong (c + a)/2$ , and a nuclear quadrupole electric moment is $Q_2=2/5Z(c^2-a^2)$, where a and c are spheroid, prolate or ellipse axes.

For the highly deformed nuclei of the $^{235}U$ and $^{238}U$ isotopes the $Q_2$ values were reported to be 10.51±0.06 and 11.15±0.05, respectively, whereas for the prolate nucleus of $^{238}U$, $\beta_2=0.261$, $\beta_4=0.087$ and $\beta_6=0.0$[30].

For the uranium isotopes in question, the half density radius, $R_{ch}$, was reported to increase with A from 7.043±0.008 fm for $^{235}U$ to 7.076±0.006 fm for $^{238}U$ [30] which results from the fit to the muonic 2p-1s and 3d-2p transition energies in the muonic isotopes of $^{235}U$ and $^{238}U$. The <r>-expectation value of the 1s muon orbital, as for all the muon orbital radii, due to the muon/electron mass ratio, is by about 200 times smaller than the respective electronic orbital value. Therefore, the 1s muons, as "immersed" in the "transparent" heavy nuclei (muons and electrons are not subjected to strong nuclear interactions), are very sensitive to the nuclear charge distribution. In case of uranium, of the high Z value, the 1s muons are estimated to spend more than half their time inside the nucleus (and accordingly less time in case of the 1s electrons in the nuclei of the respective electronic uranium isotopes).

For the major uranium isotope nuclei, a thickness of the nuclear charge skin, 4aln3, where a is 0.454±0.006 fm for $^{235}U$ and 0.448±0.004 fm for $^{238}U$ [30], is equal to 1.995 fm and 1.969 fm, respectively, whereas the $r_0$ value from Eq.(3) amounts to about 1.14 fm.

The nonspherical shape of the nuclear quadrupole field causes the Sternheimer effect, i.e. a nonspherical distribution of the core electrons that affects the electronic valence states[29,30]. In consequence, e.g. the orthogonal s and $p_{1/2}$ orbitals of some elongated shape nuclei, cannot be spherical. The Sternheimer effect should be taken into account especially in the exact relativistic calculations of the electronic configurations of the heaviest elements[12-14, 31-35] that display large nuclear deformations. The problem is that the synthesized elements of Z>99 (or perhaps for Z>100 in the future) are not available in amounts indispensable for spectral measurements, and for experimental determinations of the nuclear charge distribution either, to verify the extrapolated calculations for the transcurium elements.

## Acknowledgments

The assistance of Professor Fred Basolo to make this paper more readable and understandable is gratefully acknowledged.

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