University of Toronto

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Actinides in Solution: Nuclear Waste, Strong Correlations, and Emergence

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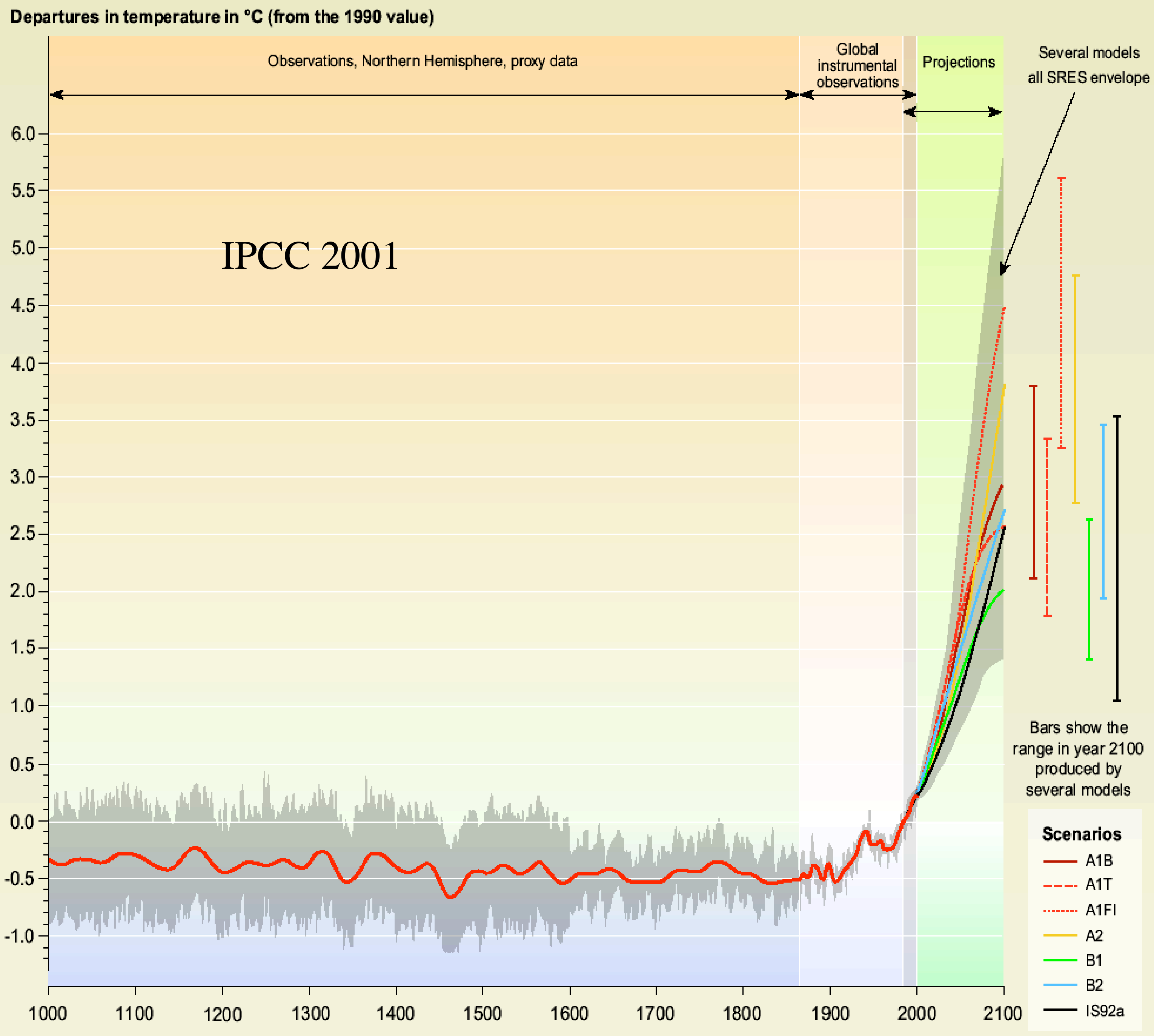
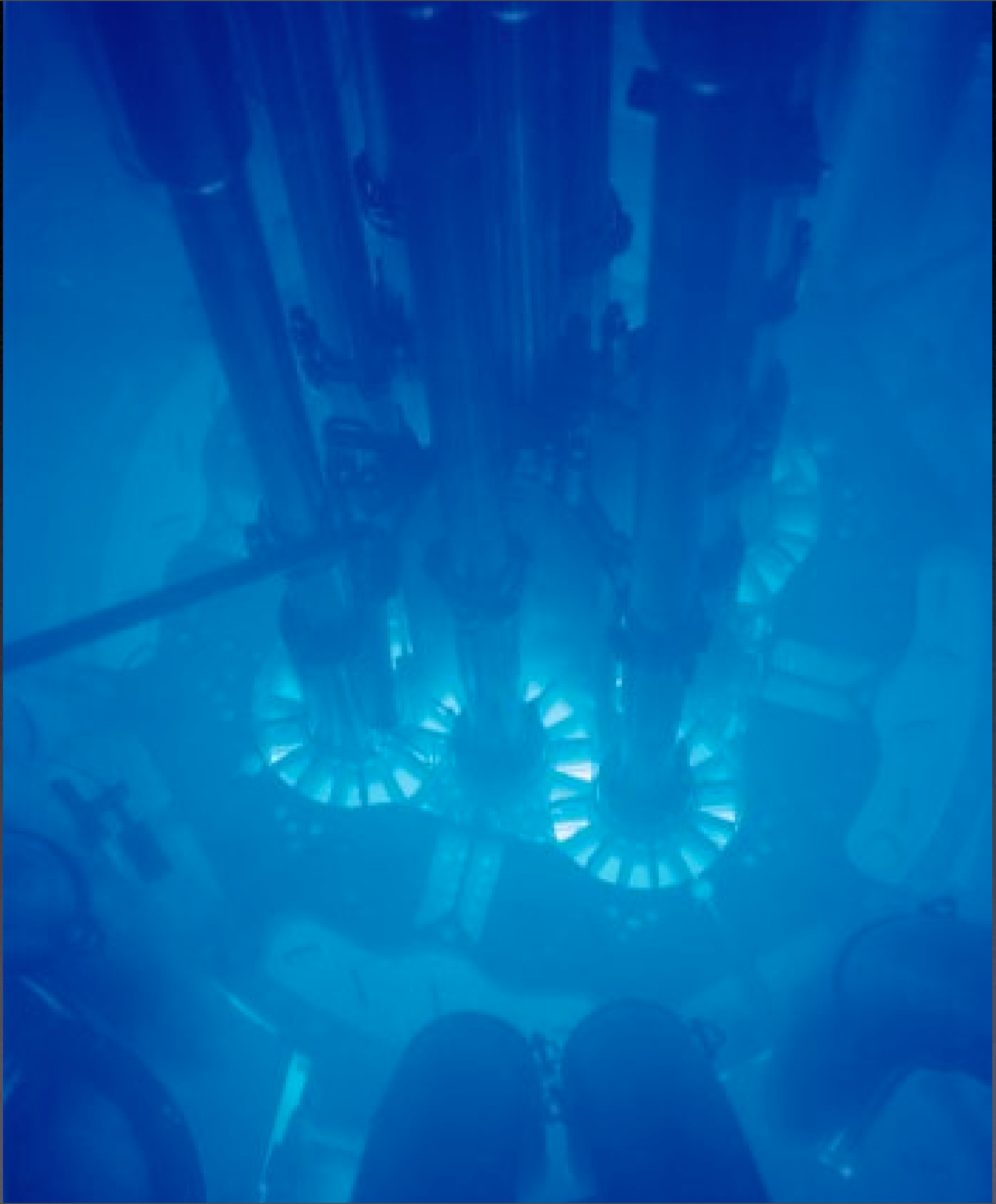
NSF DMR-0213818 / 0605619

“Migration of plutonium in ground water at the Nevada Test Site,” A. B. Kersting *et al.* Nature **397**, 56 (1999)

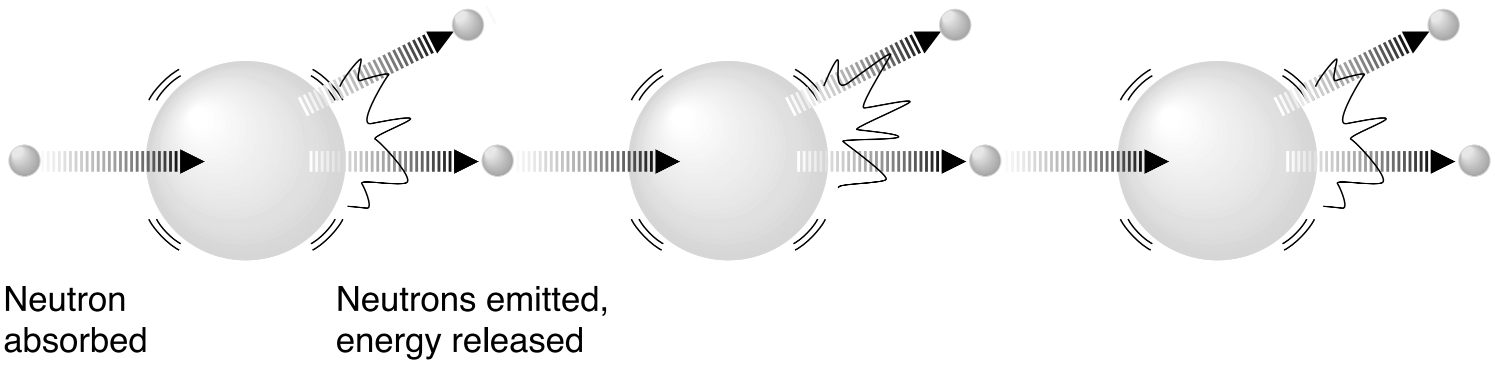
Variations of the Earth's surface temperature: years 1000 to 2100



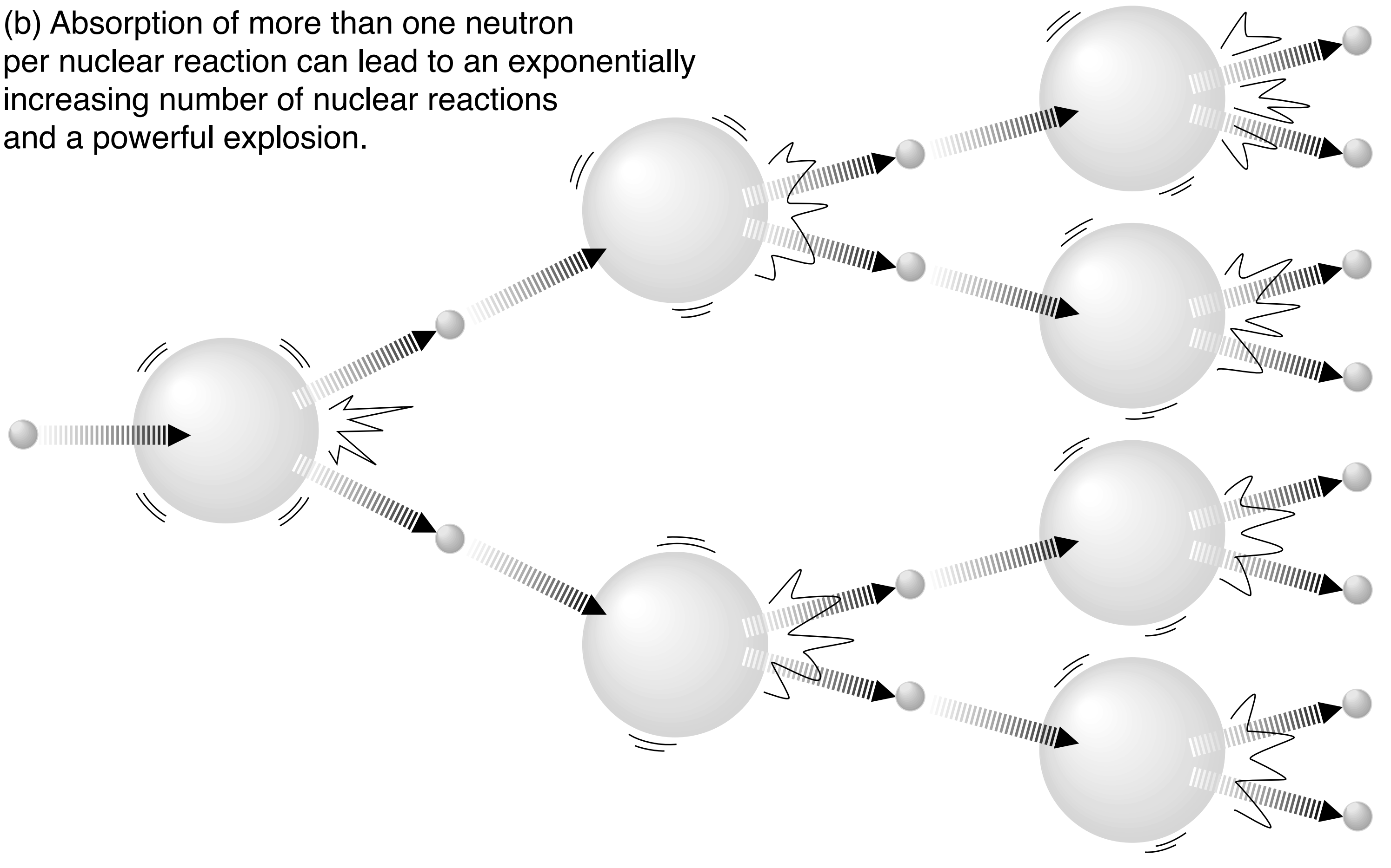
IPCC 2001



(a) Absorption of only one neutron per nuclear reaction leads to sustainable nuclear power.



(b) Absorption of more than one neutron per nuclear reaction can lead to an exponentially increasing number of nuclear reactions and a powerful explosion.

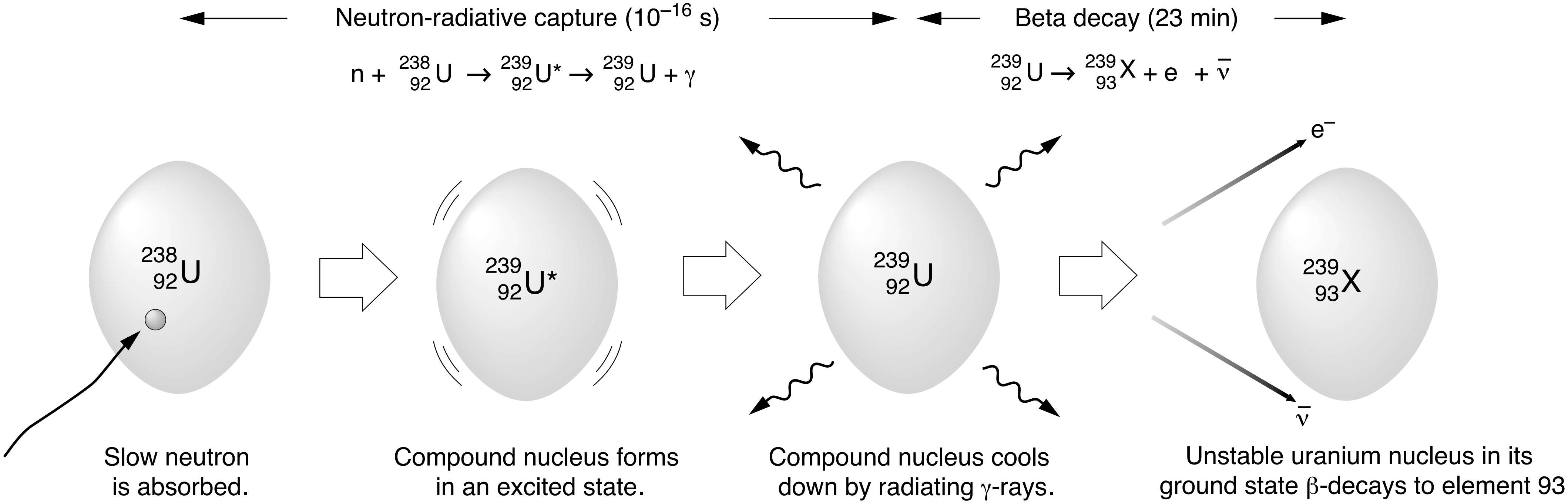


Challenges in Plutonium Science

Los Alamos Science Number 26, 2000

Volume I
Historical Introduction
Condensed-Matter Physics
Plutonium Aging

Volume II
Plutonium Metallurgy
Actinide Chemistry and the Environmen
The Yucca Mountain Project



Neutron-radiative capture (10^{-16} s)

$$n + {}^{238}_{92}U \rightarrow {}^{239}_{92}U^* \rightarrow {}^{239}_{92}U + \gamma$$

Beta decay (23 min)

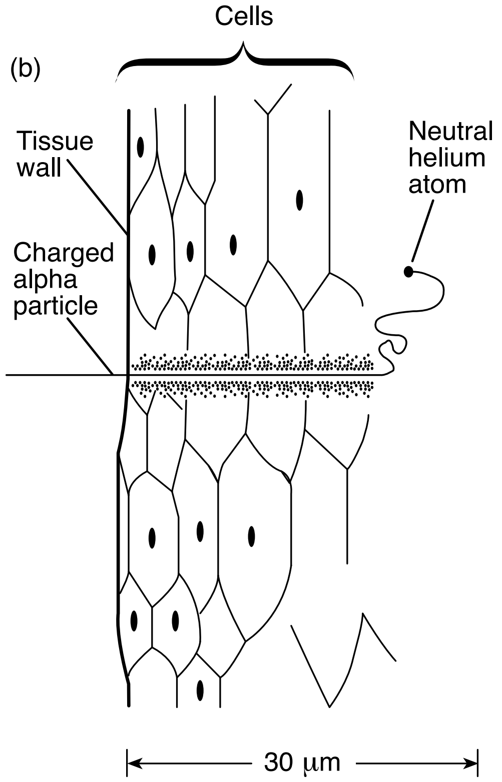
$${}^{239}_{92}U \rightarrow {}^{239}_{93}X + e + \bar{\nu}$$

Slow neutron is absorbed.

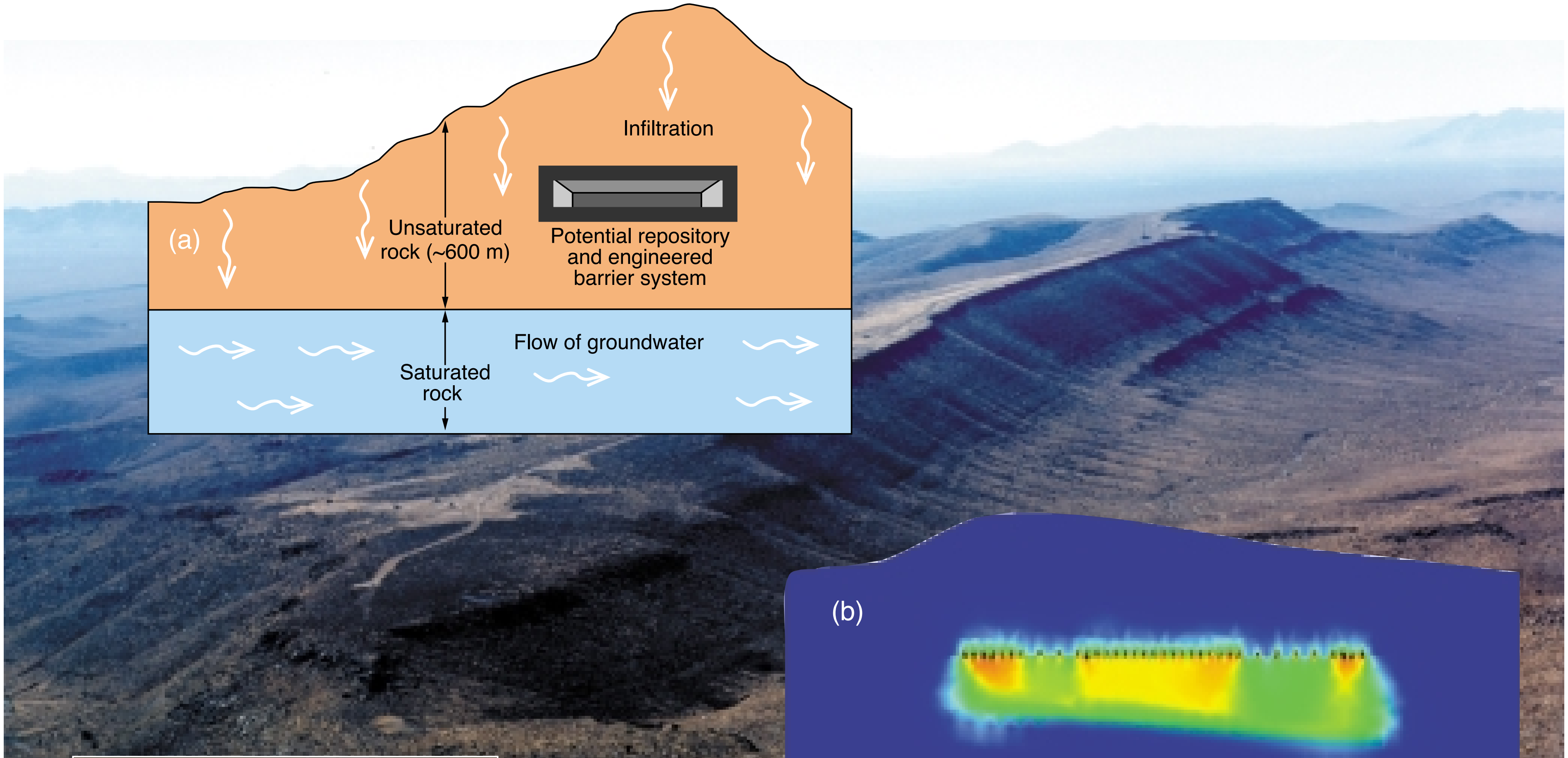
Compound nucleus forms in an excited state.

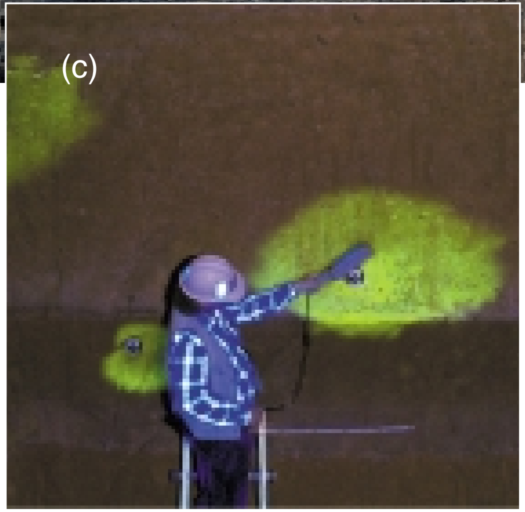
Compound nucleus cools down by radiating γ-rays.

Unstable uranium nucleus in its ground state β-decays to element 93

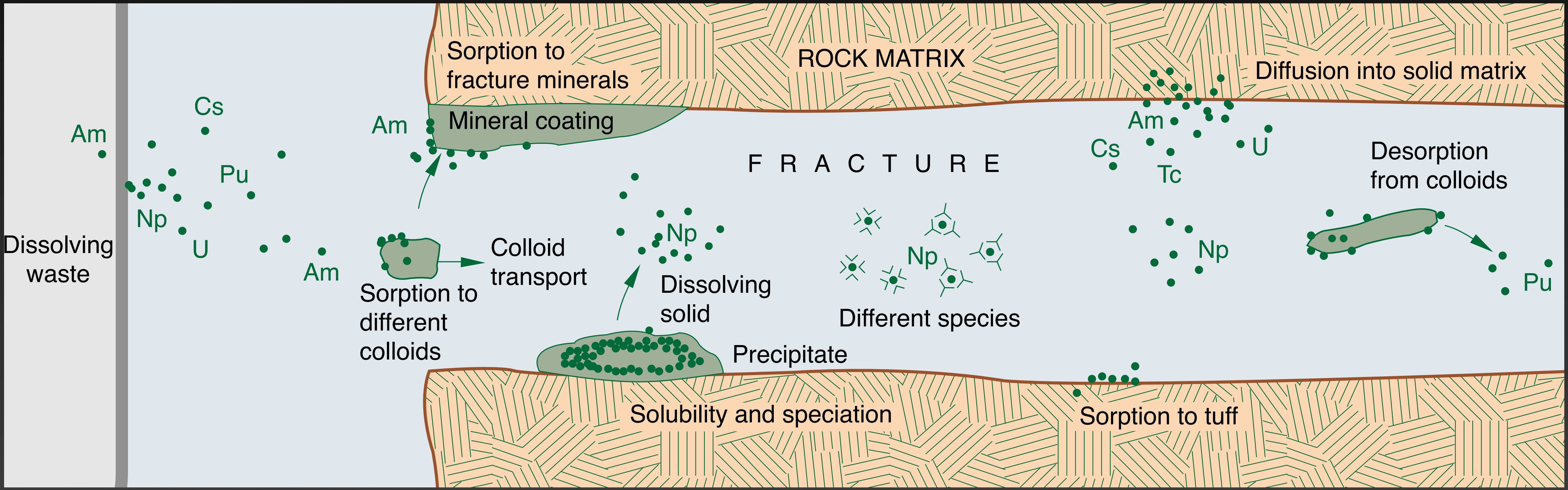


Alexander Litvinenko: ^{210}Po poisoning





The tuff itself provides desirable containment characteristics, and the fracture zones in this area contain zeolites and other minerals that have a high sorption affinity for most of the actinides. Based on extensive field data and state-of-the-art modeling of worst-case scenarios, researchers have predicted that the waste would take at least 10,000 years to migrate to the water table (saturated zone). This prediction is consistent with experience at the nearby Nevada Test Site, which indicates that the mobility of radionuclides is generally very small—that is, for the most part, the actinides injected into underground test holes from nuclear explosions have remained close to where they were deposited. However, recent



Dissolving waste

Sorption to fracture minerals

Mineral coating

ROCK MATRIX

Diffusion into solid matrix

FRACTURE

Sorption to different colloids

Colloid transport

Dissolving solid

Precipitate

Different species

Desorption from colloids

Solubility and speciation

Sorption to tuff


Pu(III)
Pu(IV) $HClO_4$
Pu(V)
Pu(VI)
Pu(VII)
Pu(IV) HCl
Pu(IV) $HClO_4$
Pu(IV) HNO_3
Pu(IV) colloid

Photo: LBL

Outline

- Actinides in solution
- Disproportionation and negative-U
- 5f orbitals are chemically active due to relativity
- Density functional theory calculations
- Inclusion of spin-orbit interaction & strong correlations
- Environmental chemistry of Yucca Mountain
- Conclusions and open questions

Reduction-Oxidation (Redox) Electrochemistry Primer

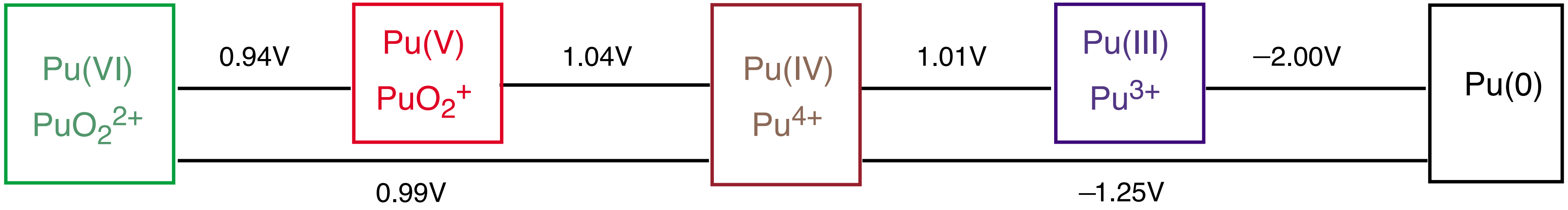
$$H_2(g) + F_2(g) \rightarrow 2\ H\ F \rightarrow 2H^+(aq) + 2F^-(aq)$$

← oxidizing half-reactions reducing →

$$F_2(g) + 2e^- \rightarrow 2\ F^-(aq) \qquad 2.87\ V$$

$$2\ H^+(aq) + 2e^- \rightarrow H_2(g) \qquad 0\ V$$

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad -2.71\ V$$



Pu(VI) PuO_2^{2+}

0.94V

Pu(V) PuO_2^{+}

1.04V

Pu(IV) Pu^{4+}

1.01V

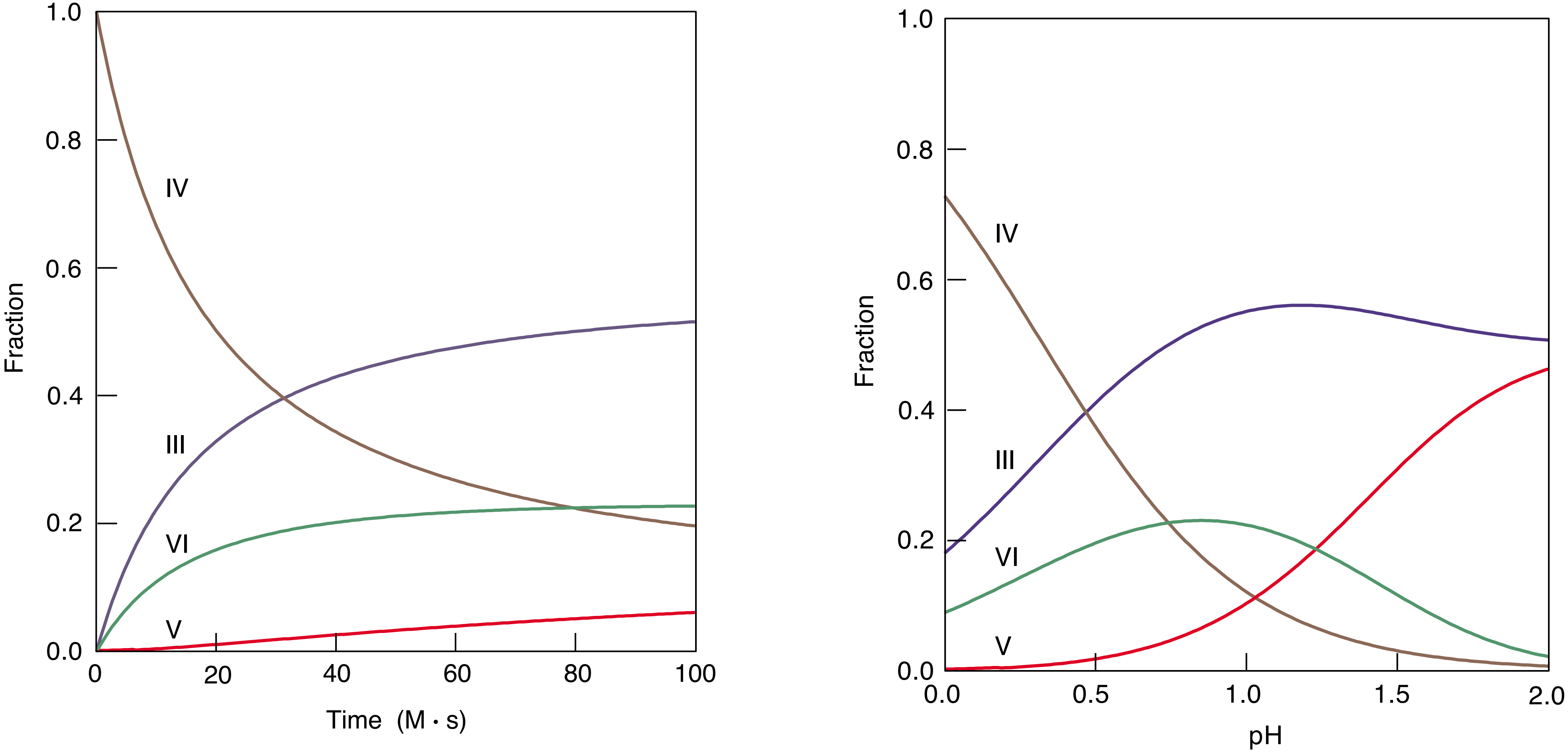
Pu(III) Pu^{3+}

−2.00V

Pu(0)

0.99V

−1.25V



David Clark, “The Chemical Complexities of Plutonium,” in *Los Alamos Science: Challenges in Plutonium Science* Vol. II No. 26 (2000).

“Formal” Oxidation States

Table I. Oxidation States of Light Actinides[a]

Th	Pa	U	Np	Pu	Am	Cm
III	III	III	III	III	**III**	**III**
IV	IV	**IV**	IV	**IV**	IV	IV
	V	V	**V**	**V**	V	
		VI	VI	**VI**	VI	
			VII	VII		

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[a] The environmentally most important oxidation states are bolded.

W. Runde, “The Chemical Interactions of Actinides in the Environment,” in *Los Alamos Science: Challenges in Plutonium Science* Vol. II No. 26 (2000).

Disproportionation Reactions

$$2\ \mathrm{E}^{n+} \rightarrow \mathrm{E}^{(n+1)+} + \mathrm{E}^{(n-1)+}$$

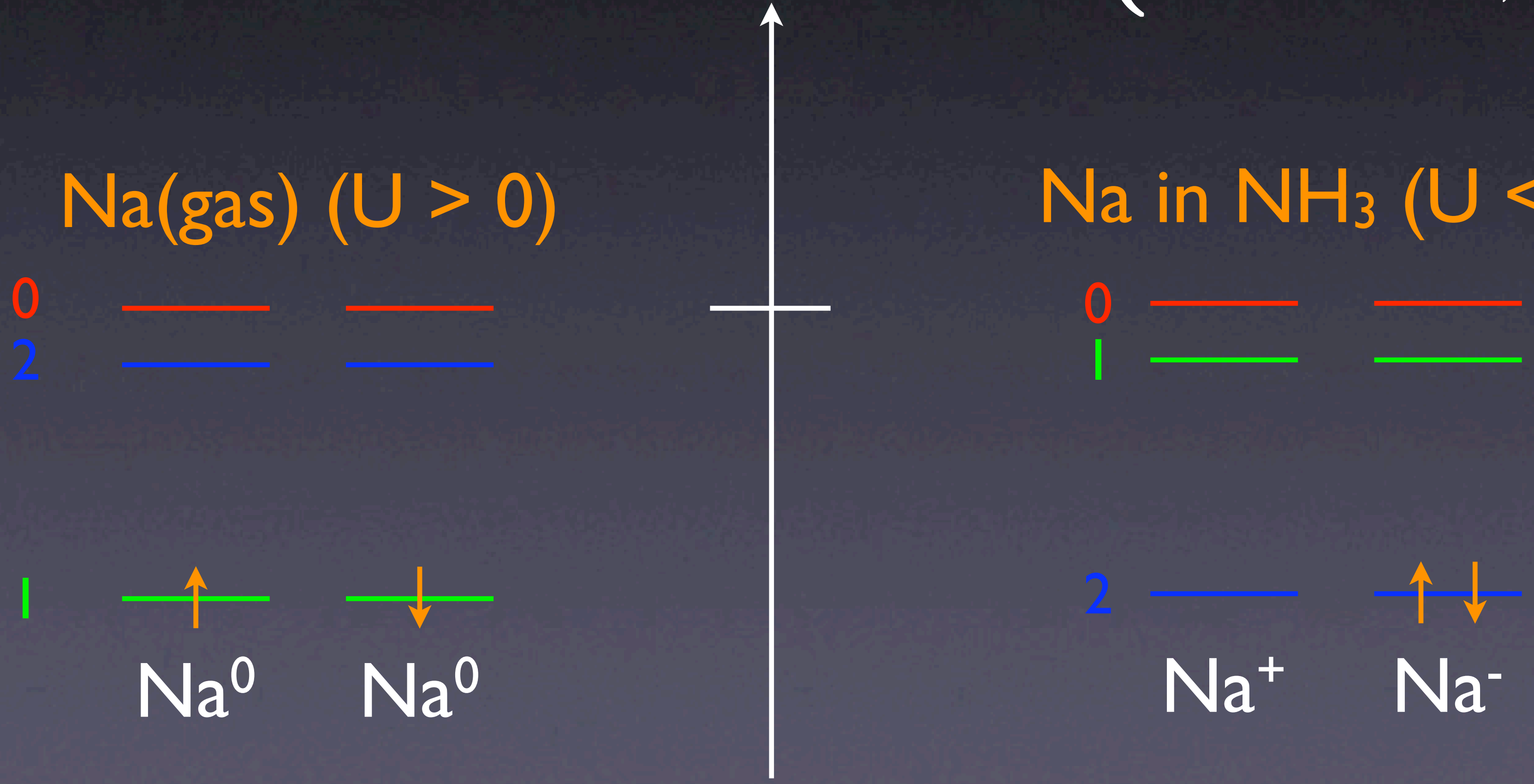
$$\begin{aligned}
2\mathrm{Pu}^{4+} + 2\mathrm{H_2O} \quad &\leftrightarrow \quad \mathrm{Pu}^{3+} + \mathrm{PuO_2}^{+} + 4\mathrm{H}^{+} \\
\mathrm{Pu}^{4+} + \mathrm{PuO_2}^{+} \quad &\leftrightarrow \quad \mathrm{Pu}^{3+} + \mathrm{PuO_2}^{2+} \\
2\mathrm{PuO_2}^{+} + 4\mathrm{H}^{+} \quad &\leftrightarrow \quad \mathrm{Pu}^{4+} + \mathrm{PuO_2}^{2+} + 2\mathrm{H_2O}
\end{aligned}$$

Ionization levels and negative-U

$$\hat{H}_{eff} = \epsilon_a n + U n_\uparrow n_\downarrow$$

“Atomic” limit of Hubbard model

$$E_0 = \begin{cases} 0, & n = 0 \\ \epsilon_a, & n = 1 \\ 2\epsilon_a + U, & n = 2 \end{cases}$$



Na(gas) (U > 0)

0

2

1

Na^0 Na^0

Na in NH_3 (U < 0)

0

1

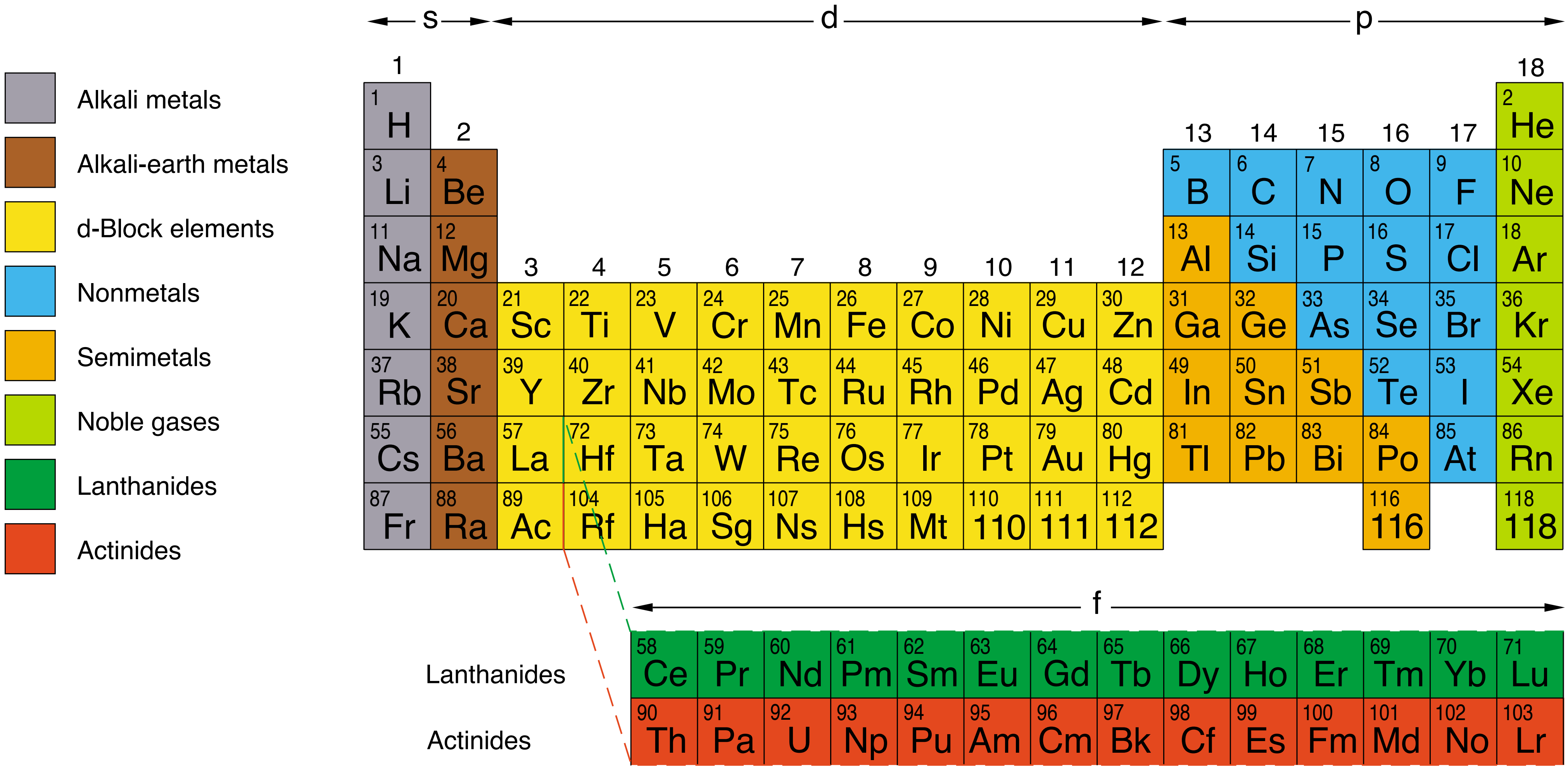
2

Na^+ Na^-

Examples of negative-U

- Alkali metals in liquid ammonia
- Other metal ions in aqueous solution: In^{2+} and Sn^{3+}
- Doped chalcogenide glasses [P. W. Anderson 1975]
- Indium in lead telluride
- Interstitial boron or vacancies in silicon (Watkins)

G. D. Watkins, “Negative-U properties for defects in solids” Festkörperprobleme (Advances in Solid State Physics) XXIV, p.163 P. Grosee (ed.) (Vieweg, Braunschweig 1984).

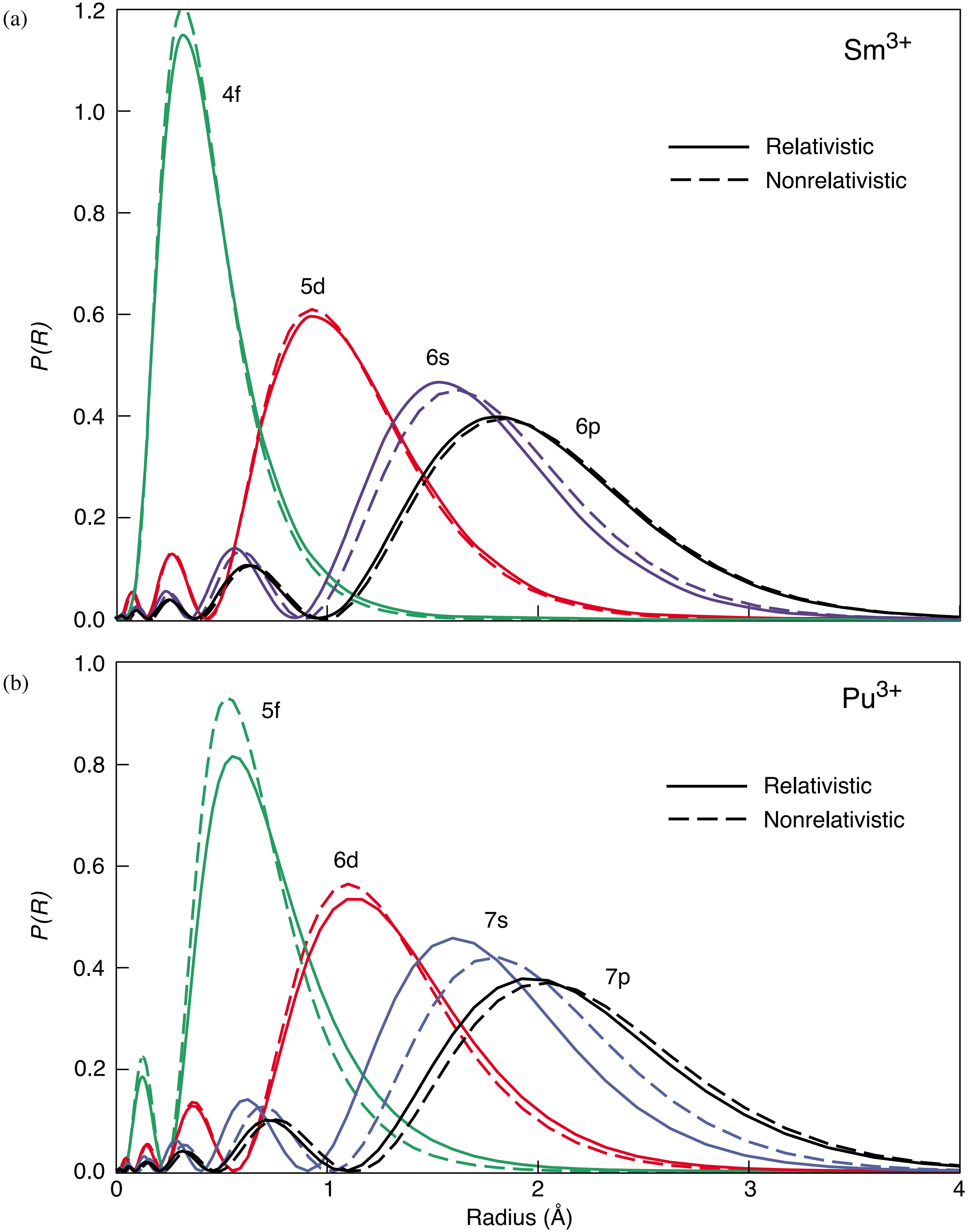


- Alkali metals
- Alkali-earth metals
- d-Block elements
- Nonmetals
- Semimetals
- Noble gases
- Lanthanides
- Actinides

s		d										p					
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112				116 116		118 118

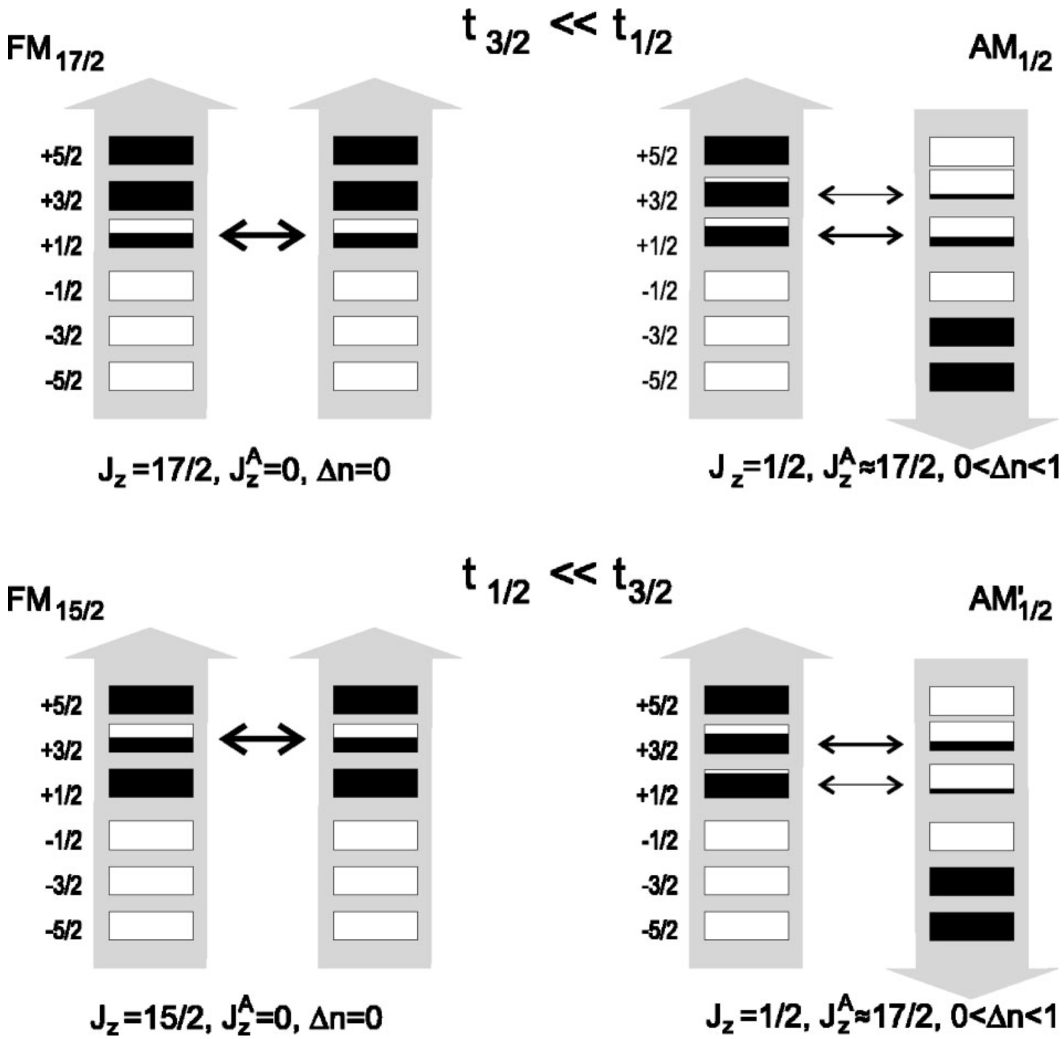
	f													
Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Actinide		**Configuration**		
Ac	actinium		$6d^1$	$7s^2$
Th	thorium		$6d$	$7s^2$
Pa	protactinium	$5f^2$	$6d^1$	$7s^2$
U	uranium	$5f^3$	$6d^1$	$7s^2$
Np	neptunium	$5f^4$	$6d^1$	$7s^2$
Pu	plutonium	$5f^6$		$7s^2$
Am	americium	$5f^7$		$7s^2$
Cm	curium	$5f^7$	$6d^1$	$7s^2$
Bk	berkelium	$5f^9$		$7s^2$
Cf	californium	$5f^{10}$		$7s^2$
Es	einsteinium	$5f^{11}$		$7s^2$
Fm	fermium	$5f^{12}$		$7s^2$
Md	mendelevium	$5f^{13}$		$7s^2$
No	nobelium	$5f^{14}$		$7s^2$
Lr	lawrencium	$5f^{14}$	$6d^1$	$7s^2$



$$a_0 = \frac{\hbar^2}{me^2}$$

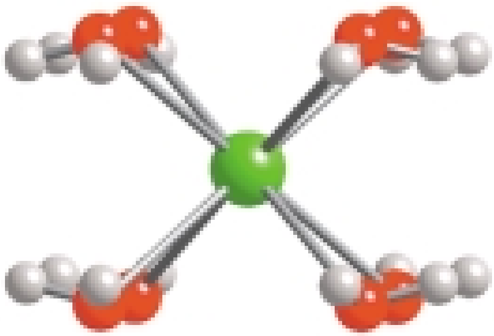
Disproportionation in a Model of Partially Localized 5f Electrons



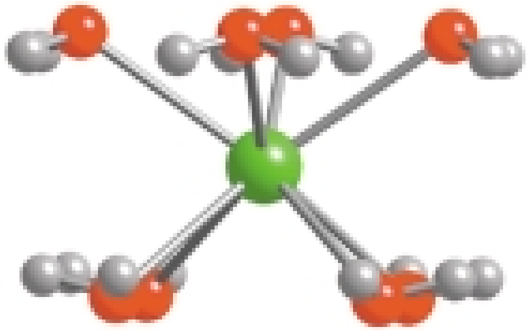
"Approximate treatment of 5f-systems with partial localization due to intra-atomic correlations," E. Runge, P. Fulde, *et al.*, Phys. Rev. B**69**, 155110 (2004)

XAFS = X-ray Absorption Fine Structure

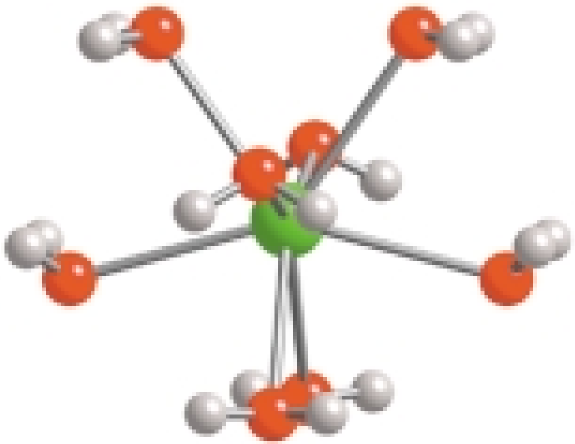
(a) Pu(III,IV): Cube



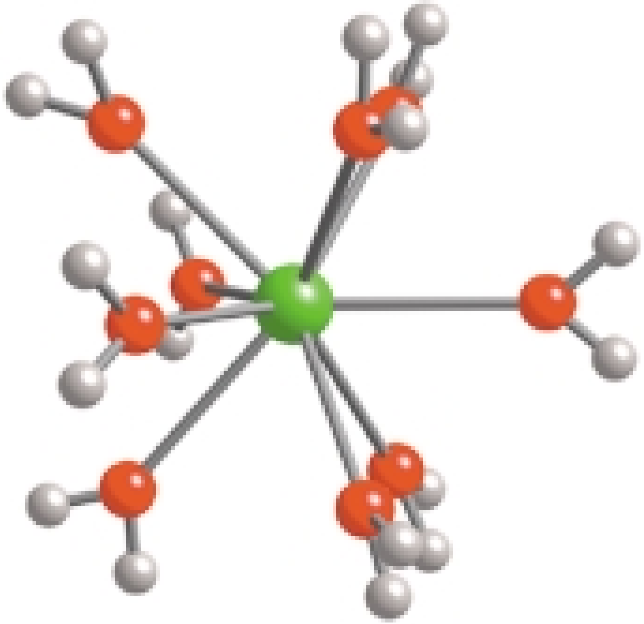
Pu(III,IV): Square antiprism



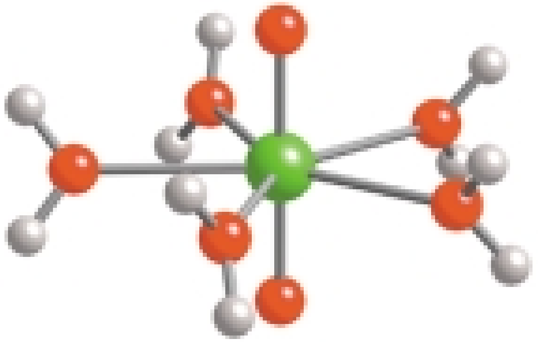
Pu(III,IV): Dodecahedron



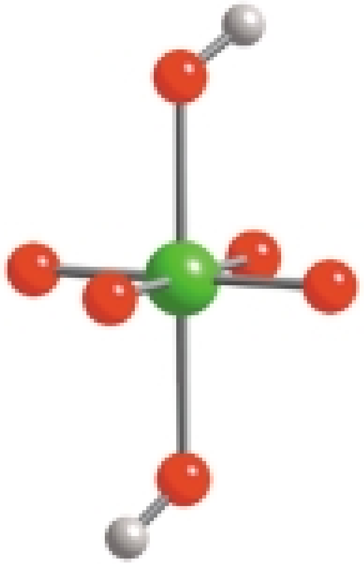
(b) Pu(III,IV): Tricapped trigonal prism



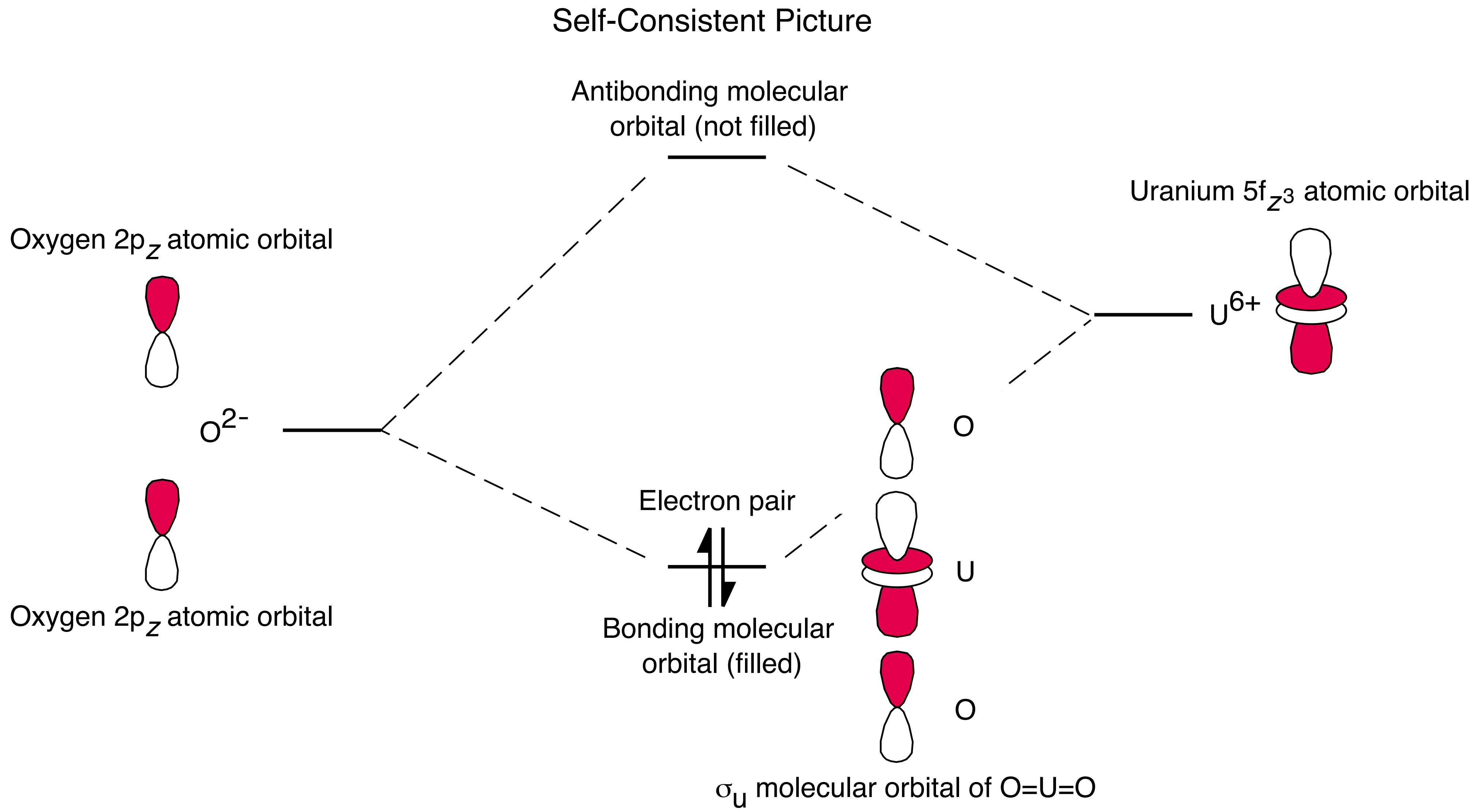
(c) Pu(V,VI): Pentagonal bipyramid



(d) Pu(VII): Tetragonal bipyramid



O=An=O Actinyl Ion



P. J. Hay and R. L. Martin, “Computational Studies of Actinide Chemistry,” in *Los Alamos Science: Challenges in Plutonium Science* Vol. II No. 26 (2000).

Redox Reactions

$$\mathrm{PuO_2(H_2O)_5^{2+}(VI)} + \tfrac{1}{2}\ \mathrm{H_2(g)} + \mathrm{H_2O} \rightarrow \mathrm{PuO_2(H_2O)_5^{+}(V)} + \mathrm{H_3O^+}$$

$$\mathrm{Pu(H_2O)_8^{4+}(IV)} + \tfrac{1}{2}\ \mathrm{H_2(g)} + \mathrm{H_2O} \rightarrow \mathrm{Pu(H_2O)_8^{3+}(III)} + \mathrm{H_3O^+}$$

$$\mathrm{PuO_2(H_2O)_5^{+}(V)} + 3\ \mathrm{H_3O^+} + \tfrac{1}{2}\ \mathrm{H_2(g)} \rightarrow \mathrm{Pu(H_2O)_8^{4+}(IV)} + 2\ \mathrm{H_2O}$$

Density Functional Theory (DFT)

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$n(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r_2}, \ldots, \vec{r_N})|^2 \; d^3r_2 d^3r_3 \cdots d^3r_N$$

$$E[n(\vec{r})] = \langle\Psi|\hat{H}|\Psi\rangle$$

DFT Ingredients

- Use ADF (www.scm.com) with n=4 frozen cores
- Scalar ZORA relativity (spin orbit included later)
- Unrestricted spin
- Revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional
- Geometry relaxation
- Vibrational modes contribute to free energy
- First solvation sphere treated quantum mechanically
- Beyond first solvation sphere: use “conductor-like screening” (COSMO) solvation model

Zero Order Regular Approximation (ZORA)

$$E = \sqrt{m_0^2 c^4 + \vec{p}^2 c^2} + V(\vec{r})$$

$$\begin{aligned}
\tilde{E} &\equiv E - m_0 c^2 \\
&= m_0 c^2 \left(\sqrt{1 + \frac{\vec{p}^2}{m_0^2 c^2}} - 1 \right) + V(\vec{r}) \\
&\approx \frac{\vec{p}^2}{2m_0} - \frac{\vec{p}^4}{8 m_0^3 c^2} + \ldots + V(\vec{r})
\end{aligned}$$

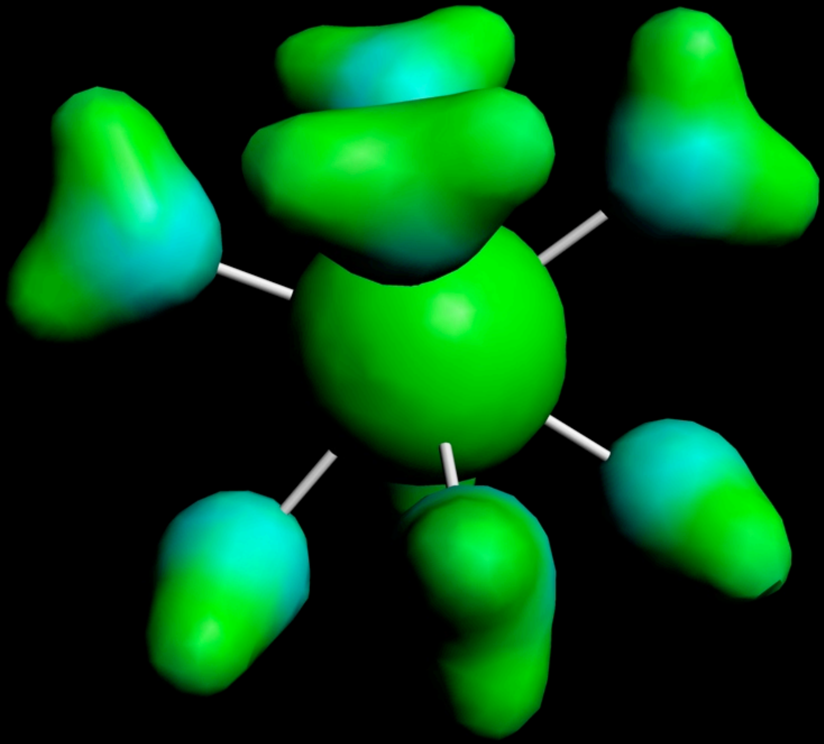
$$|\vec{p}| < m_0 c$$

$$E \quad < \quad 2m_0c^2 - V(\vec{r})$$

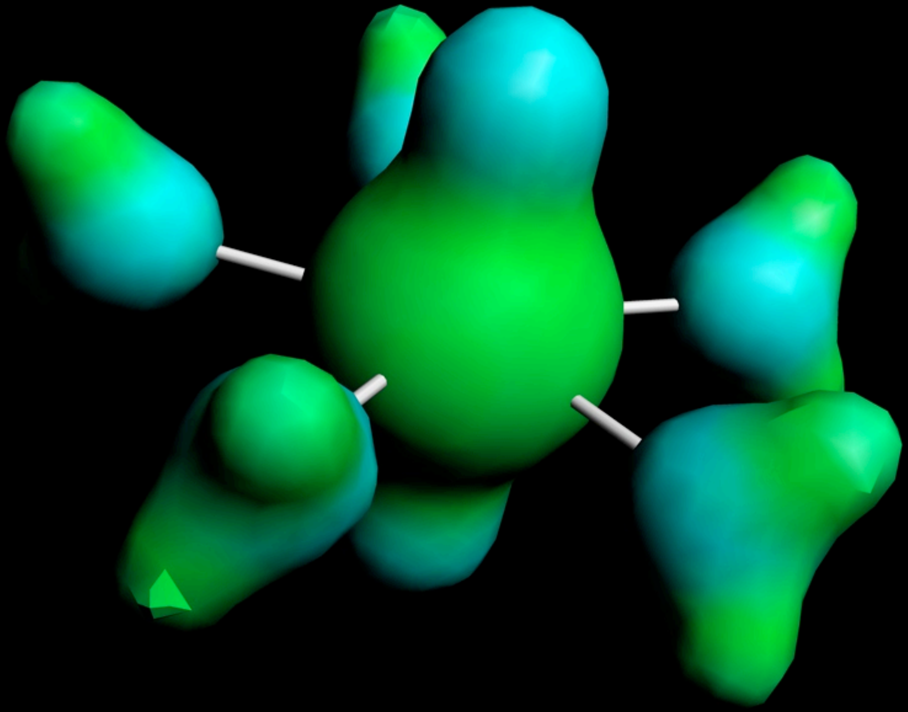
$$V(\vec{r}) \quad \sim \quad -\frac{Ze^2}{r}$$

$$\begin{aligned}
\tilde{E} \quad &= \quad \sqrt{m_0^2c^4 + \vec{p}^2c^2} - m_0c^2 + V(\vec{r}) \\
&= \quad \frac{\vec{p}^2c^2}{m_0c^2 + \sqrt{m_0^2c^4 + \vec{p}^2c^2}} + V(\vec{r}) \\
&= \quad \frac{\vec{p}^2c^2}{2m_0c^2 + \tilde{E} - V(\vec{r})} + V(\vec{r}) \\
&= \quad \frac{\vec{p}^2c^2}{(2m_0c^2 - V(\vec{r}))\left(1 + \frac{\tilde{E}}{2m_0c^2 - V(\vec{r})}\right)} + V(\vec{r})
\end{aligned}$$

$$\tilde{E}_{\mathrm{ZORA}} \equiv \frac{\vec{p}^2c^2}{2m_0c^2 - V(\vec{r})} + V(\vec{r})$$



$Pu(H_2O)_8^{3+}$



$PuO_2(H_2O)_5^{2+}$

DFT Results

Pu-O distance (Angstroms)			
Oxidation State	Hay, Martin, & Schreckenbach	This work	Experiment (XAFS)
V	1.81	1.80	1.81
VI	1.74	1.75	1.74

Pu-OH_2 distance (Angstroms)			
Oxidation State	Hay, Martin, & Schreckenbach	This work	Experiment (XAFS)
III		2.50	2.49
IV		2.38	2.39
V	2.61	2.62	2.47
VI	2.49	2.45	2.41

DFT Results (cont.)

Reduction-Oxidation Potentials (volts) -- No spin orbit			
Reduction Reaction	Hay, Martin, & Schreckenbach	This work	Experiment
VI to V	3.19	1.70	0.95
V to IV		-0.88	1.03
IV to III		1.94	1.01

P. J. Hay, R. L. Martin, and G. Schreckenbach, "Theoretical studies of the properties and solution chemistry of AnO_2^{2+} and AnO_2^{+} aquo complexes for An = U, Np, and Pu," J. Phys. Chem. A **104**, 6259 -- 6270 (2000).

Spin-Orbit Interaction from ZORA

$$\hat{H}_{SO} = \lambda_{SO}\,\vec{\ell}\cdot\vec{s} + \alpha$$

$$\Delta E \approx \begin{cases} -0.1\ \mathrm{eV}, & j = 5/2 \\ 0.9\ \mathrm{eV}, & j = 7/2 \end{cases}$$

Redox Potentials (volts) With Spin-Orbit Interaction			
Reduction Reaction	Hay, Martin, & Schreckenbach	This work	Experiment
VI to V	3.28	0.88	0.95
V to IV		-0.42	1.03
IV to III		1.76	1.01

Shamov and Schreckenbach, J. Phys. Chem. A **109**, 10961 (2005).

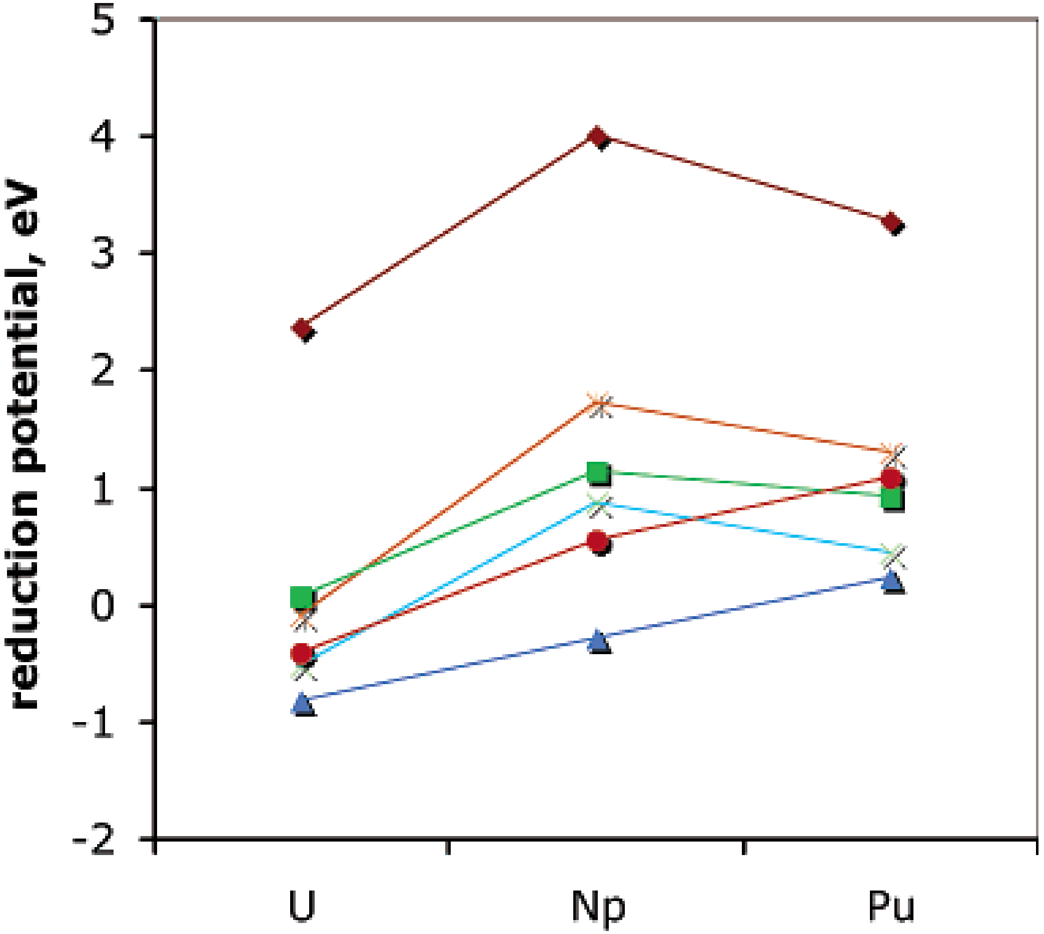


Figure 4. Calculated and experimental $[AnO_2(H_2O)_5]^{2+}/[AnO_2(H_2O)_5]^{1+}$ reduction potentials according to Table 10. Calculated values without and with the inclusion of spin−orbit and multiplet corrections are shown; see text. (Dark red diamonds) LC-ECP-B3LYP values from ref 20; (red circles and blue triangles) SC-ECP-B3LYP and Priroda-PBE values without the corrections; (orange stars and light blue crosses) SC-ECP B3LYP and Priroda PBE values with the corrections applied, correspondingly; (green squares) experimental values[87] as cited from ref 20.

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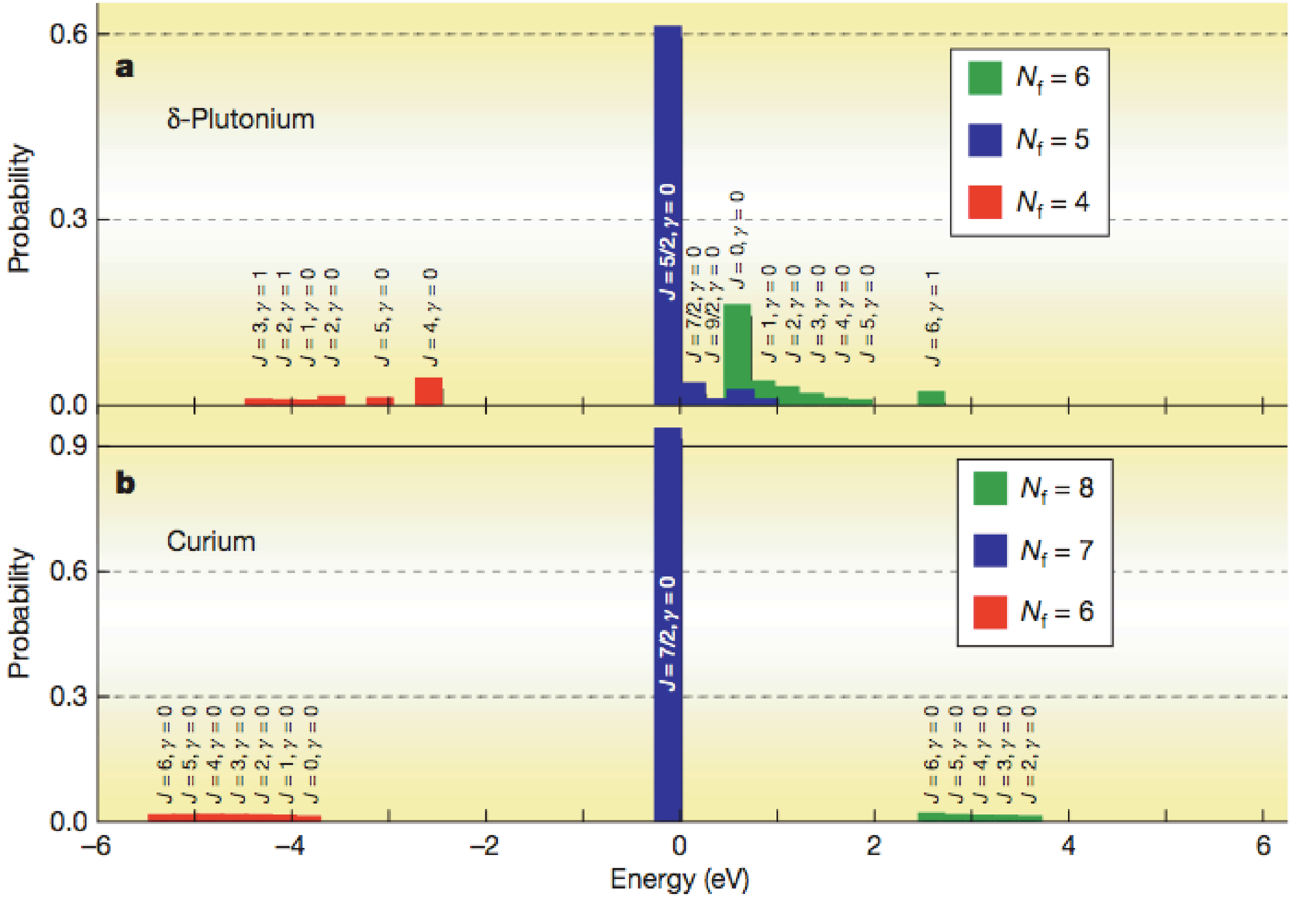
nature

LETTERS

Fluctuating valence in a correlated solid and the anomalous properties of δ-plutonium

J. H. Shim[1], K. Haule[1] & G. Kotliar[1]

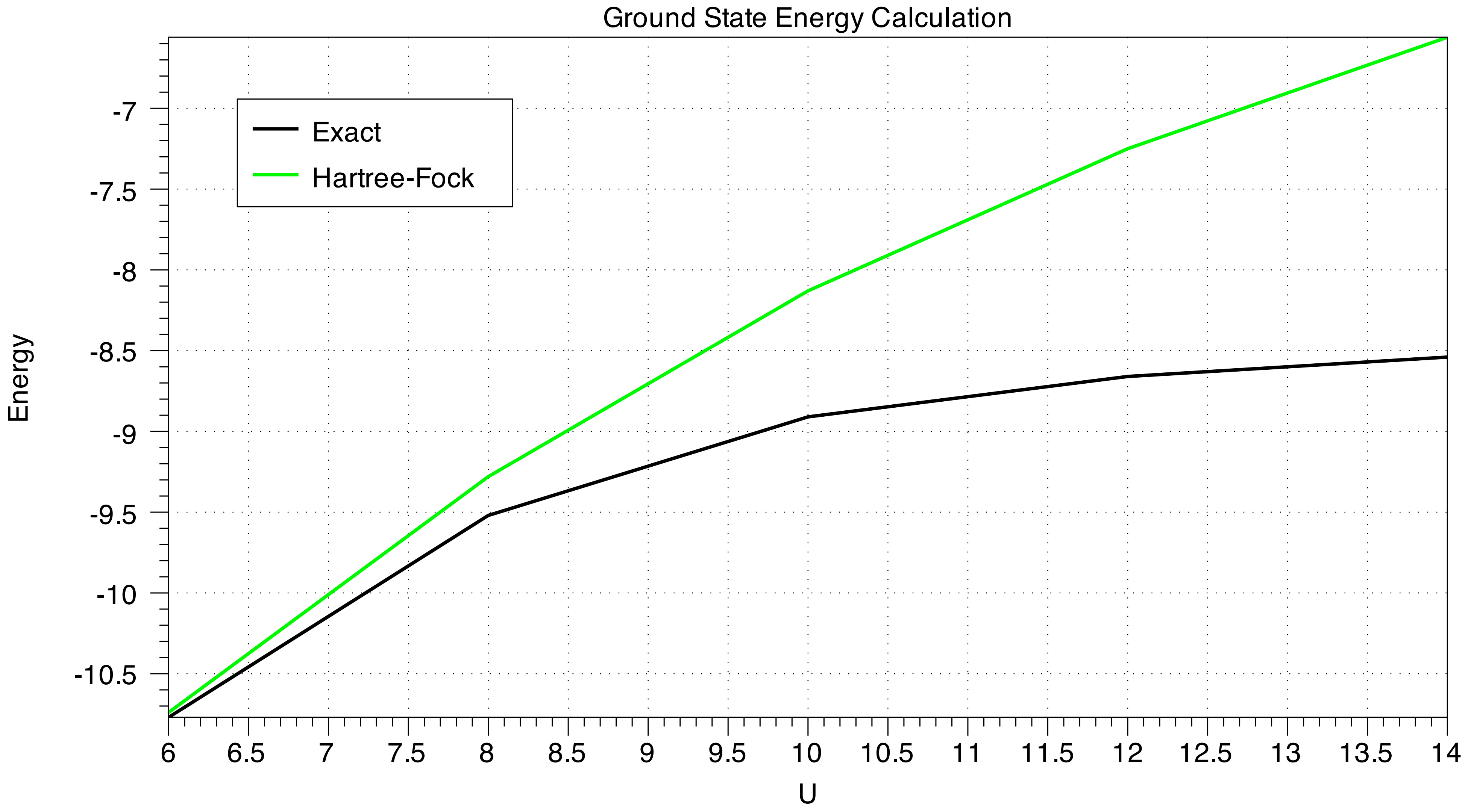


Toy Model of Strong Correlations

$$\hat{H} = e\ f^{\dagger\sigma} f_{\sigma} - t\ (f^{\dagger\sigma} c_{\sigma} + H.c.) + U\ f^{\dagger\uparrow} f^{\dagger\downarrow} f_{\downarrow} f_{\uparrow}$$

$$\begin{aligned} U f^{\dagger\uparrow} f^{\dagger\downarrow} f_{\downarrow} f_{\uparrow} &= U n_{\uparrow} n_{\downarrow} \\ &\approx U\left(\langle n_{\uparrow}\rangle n_{\downarrow} + \langle n_{\downarrow}\rangle n_{\uparrow} - \langle n_{\uparrow}\rangle\langle n_{\downarrow}\rangle\right) \\ U_{HF}(\langle n\rangle, n) &= \frac{U}{2}\langle n\rangle\ n - \frac{U}{4}\langle n\rangle^{2} \end{aligned}$$

t = 1, e = -8


Ground State Energy Calculation
Energy
U
Exact
Hartree-Fock
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
6
6.5
7
7.5
8
8.5
9
9.5
10
10.5
11
11.5
12
12.5
13
13.5
14

Strong Correlations Between 5f Electrons

M. X. LaBute, R. G. Endres, and D. L. Cox, “An Anderson impurity model for efficient sampling of adiabatic potential energy surfaces of transition metal complexes,” J. Chem. Phys. **121**, 8221 (2004).

$$\hat{H}_{el-el} = \sum_{\substack{m_1 m_2 m_3 m_4 \\ m_1+m_2=m_3+m_4}} I_{m_1,m_2,m_3,m_4} \; f^{\dagger\sigma_1}_{m_1} f^{\dagger\sigma_2}_{m_2} f_{m_3,\sigma_2} f_{m_4,\sigma_1}$$

Gaunt coefficients

$$I_{m_1,m_2,m_3,m_4} = \sum_{L=0,2,4,6} F^L \; c^{(L)}(m_1,m_4) \; c^{(L)}(m_2,m_3)$$

Slater-Condon parameters

Tight-Binding Model of Pu(5f) and O(2p) Orbitals

Kohn-Sham molecular orbitals may be expressed as a linear combination of (orthonormal) Lowdin atomic orbitals. Project onto 5f-2p subspace.

$$\hat{H} = \sum_{i,j}^{z^3, xz^2, \ldots} t_{\sigma ij}^{\sigma'} \left(f_i^{\dagger\sigma} f_{j\sigma'} + H.c. \right)$$

$Pu(H_2O)_8$: 14 independent-particle states

$PuO_2(H_2O)_5$: 26 independent-particle states

Sparse matrices with up to 500 million matrix elements

Slater-Condon Parameter $F_0 = U$

Ionization Reaction	Experiment (eV)	DFT (eV)
Pu^{3+} to $Pu^{4+} + e^-$	34.6	35.29
PuO_2^+ to $PuO_2^{2+} + e^-$	15.1(4)	15.65

Slater-Condon Parameters F_2, F_4, and F_6

M. Norman, "Calculation of effective Coulomb interaction for Pr^{3+}, U^{4+}, and UPt_3," PRB**52**, 1421 (1995)

I. S. Poirot *et al.*, "Optical study and analysis of Pu^{4+} in single crystals of $ZrSiO_4$," PRB**39**, 6388 (1989)

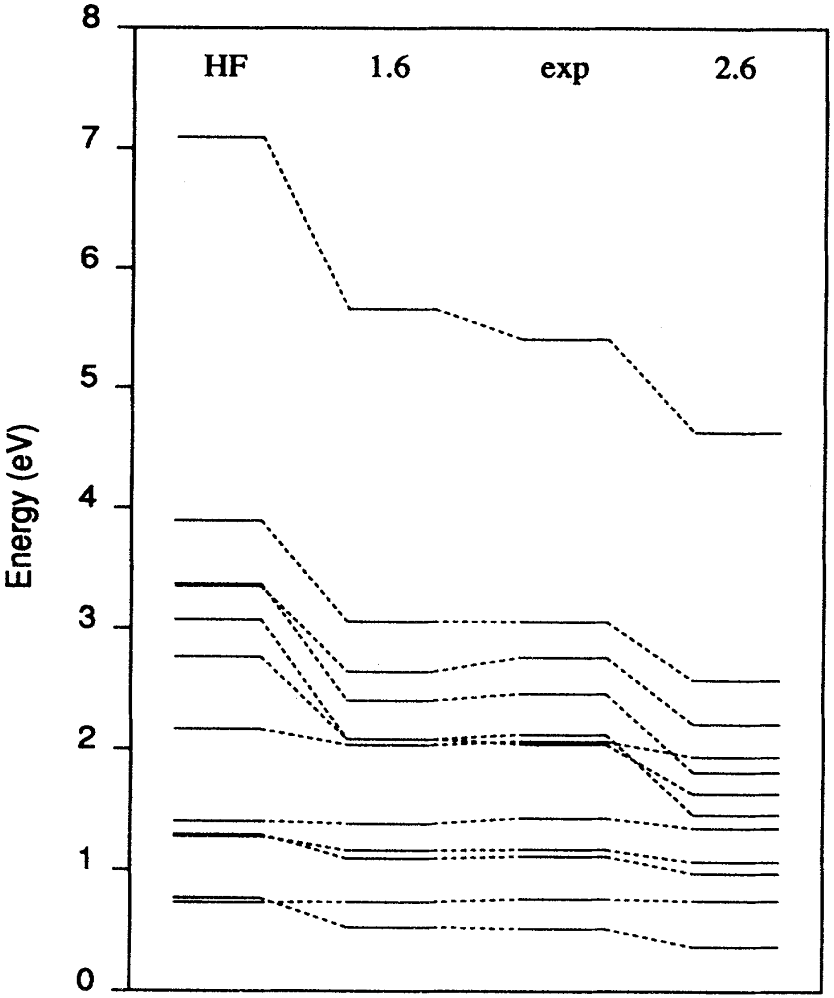


FIG. 3. Multiplet spectra (eV) relative to the $^3H_4$ ground state of U^{4+} for Hartree-Fock (HF), λ=1.6 (1.6), experiment (exp) Ref. 14, and λ=2.6 (2.6). The latter λ was fit to the observed multiplet splitting in UPt_3 (Ref. 16). The first excited state is $^3F_2$ except for Hartee-Fock, where it is $^3H_5$.

Toy Model of System / Environment

$$\hat{H} = e\ f^{\dagger\sigma} f_\sigma - t\ (f^{\dagger\sigma} c_\sigma + H.c.) + U\ f^{\dagger\uparrow} f^{\dagger\downarrow} f_\downarrow f_\uparrow$$

$$\begin{aligned} U f^{\dagger\uparrow} f^{\dagger\downarrow} f_\downarrow f_\uparrow &= U n_\uparrow n_\downarrow \\ &\approx U\left(\langle n_\uparrow\rangle n_\downarrow + \langle n_\downarrow\rangle n_\uparrow - \langle n_\uparrow\rangle\langle n_\downarrow\rangle\right) \\ U_{HF}(\langle n\rangle, n) &= \frac{U}{2}\langle n\rangle\ n - \frac{U}{4}\langle n\rangle^2 \end{aligned}$$

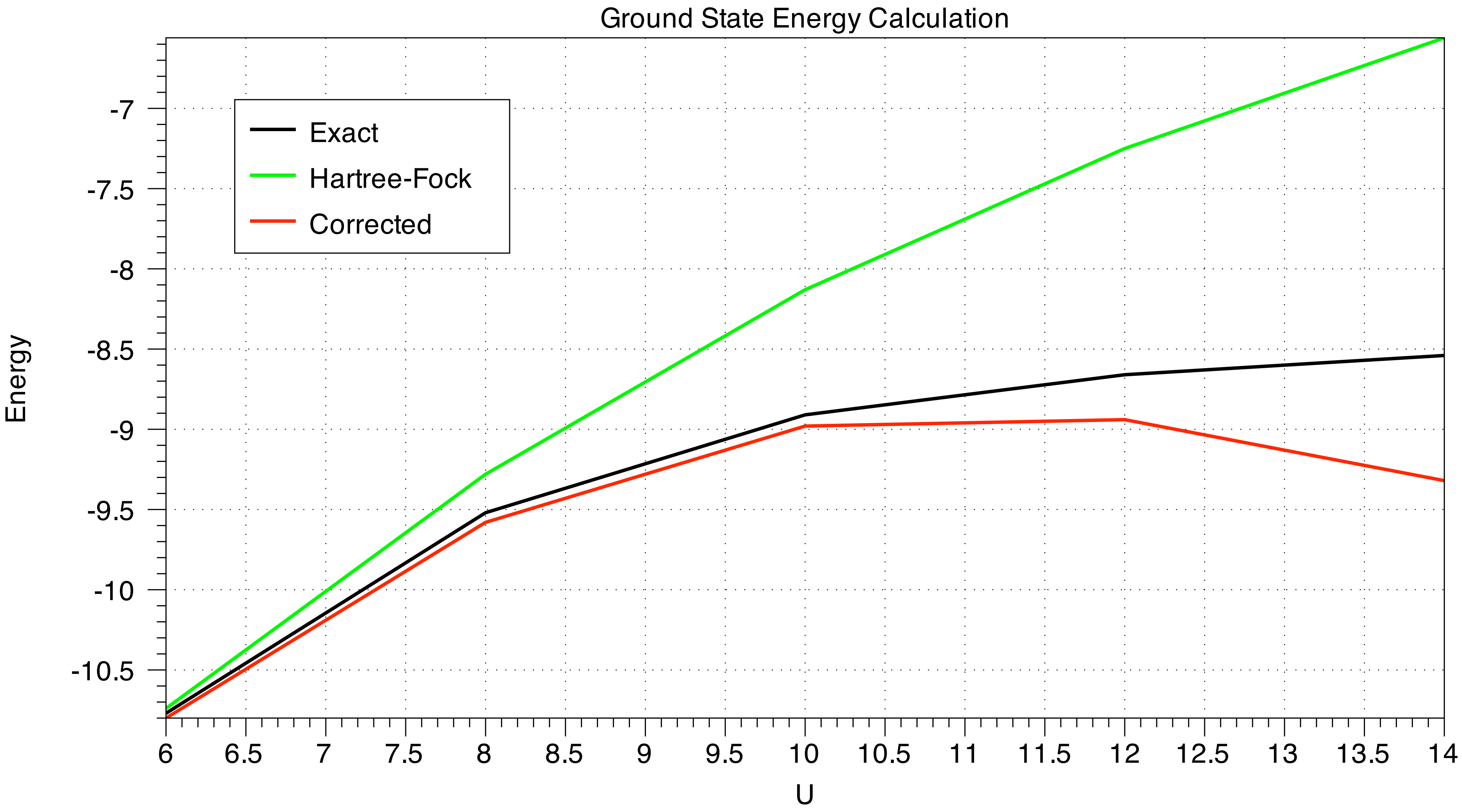
$$E_0^{corrected}(n) = E_0^{HF} - U_{HF}(\langle n \rangle, n) + \frac{U}{2}(n^2 - n)$$

$$\langle n \rangle \quad = \quad 1 + x$$

$$E_0^{corrected} \quad = \quad (1-x)E_0^{corrected}(1) + xE_0^{corrected}(2)$$

t = 1, e = -8

U	Exact	<n>	HF	E(1)	E(2)	E
6	-10.77	1.79	-10.74	-11.29	-10.68	-10.80
8	-9.52	1.61	-9.28	-10.53	-8.98	-9.58
10	-8.91	1.42	-8.13	-7.28	-10.20	-8.98
12	-8.66	1.25	-7.25	-10.06	-5.55	-8.94


Ground State Energy Calculation
Exact
Hartree-Fock
Corrected
Energy
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
6
6.5
7
7.5
8
8.5
9
9.5
10
10.5
11
11.5
12
12.5
13
13.5
14
U

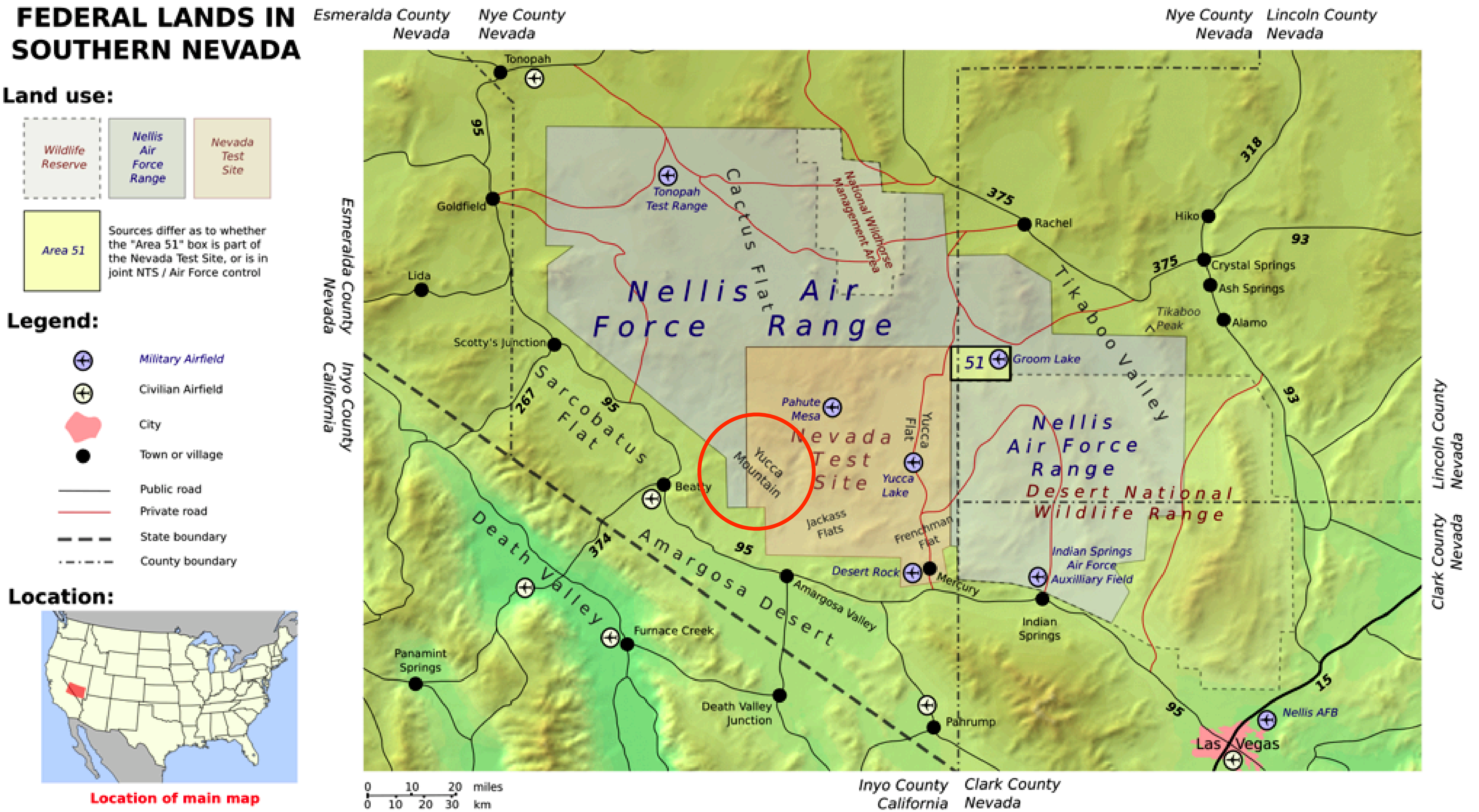
Strong Correlations Alter Redox Potentials

$$f^{\dagger\sigma_1}_{m_1} f_{m_3\sigma_2} \rightarrow f^{\dagger\sigma_1}_{m_1} f_{m_3\sigma_2} - \langle f^{\dagger\sigma_1}_{m_1} f_{m_3\sigma_2} \rangle_0$$

$$\langle \hat{H}_{el-el} \rangle_0 = 0$$

Redox Potentials From Hubbard Model			
Model	VI to V (volts)	V to IV (volts)	IV to III (volts)
DFT + SO	0.88	-0.42	1.76
Hubbard (F_0 = 3 eV)	-0.08	1.05	0.70
Experiment	0.95	1.03	1.01

Yucca Mountain



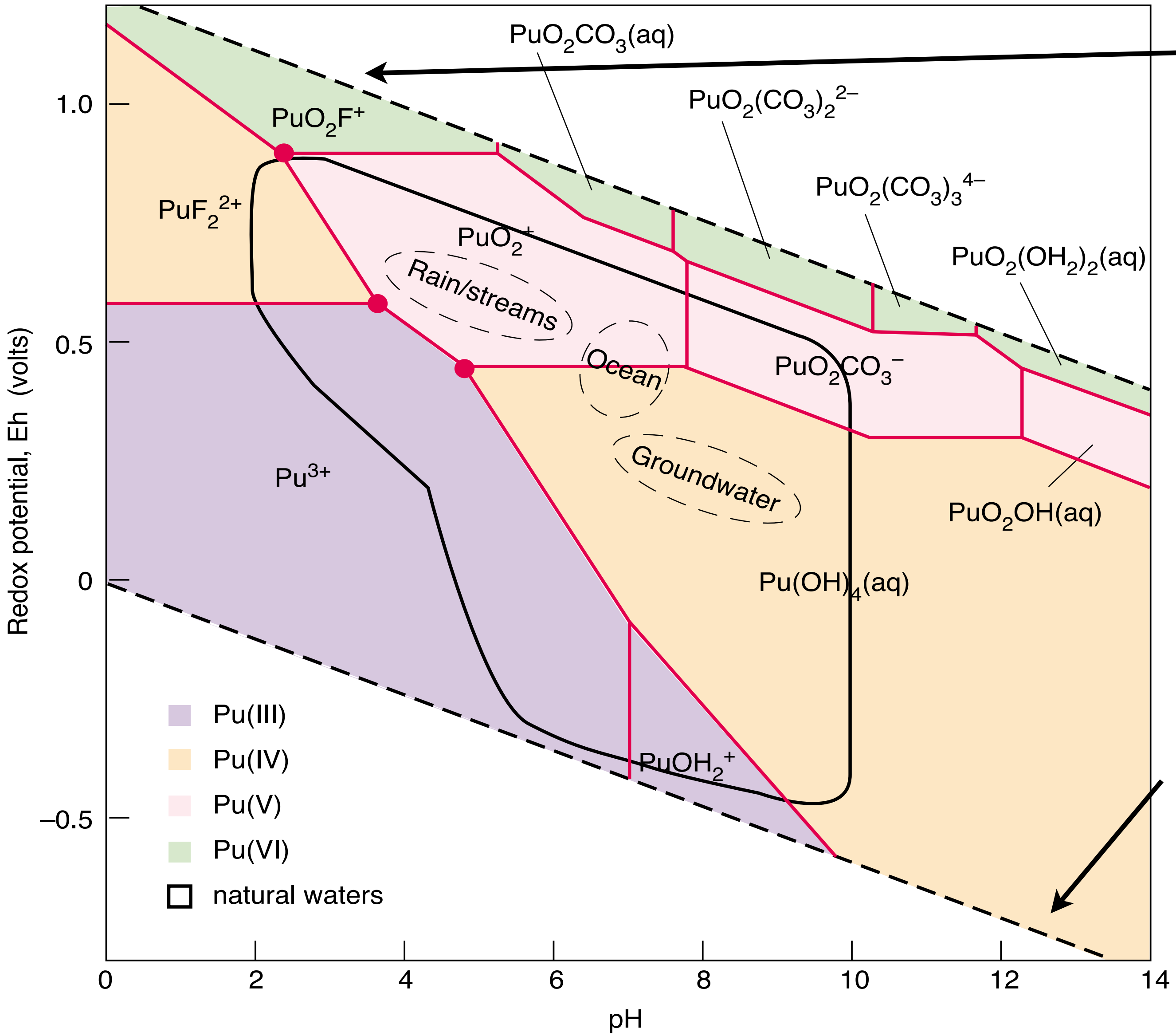
Sources differ as to whether the "Area 51" box is part of the Nevada Test Site, or is in joint NTS / Air Force control


DANGER

Complexation Follows Effective Ion Charge

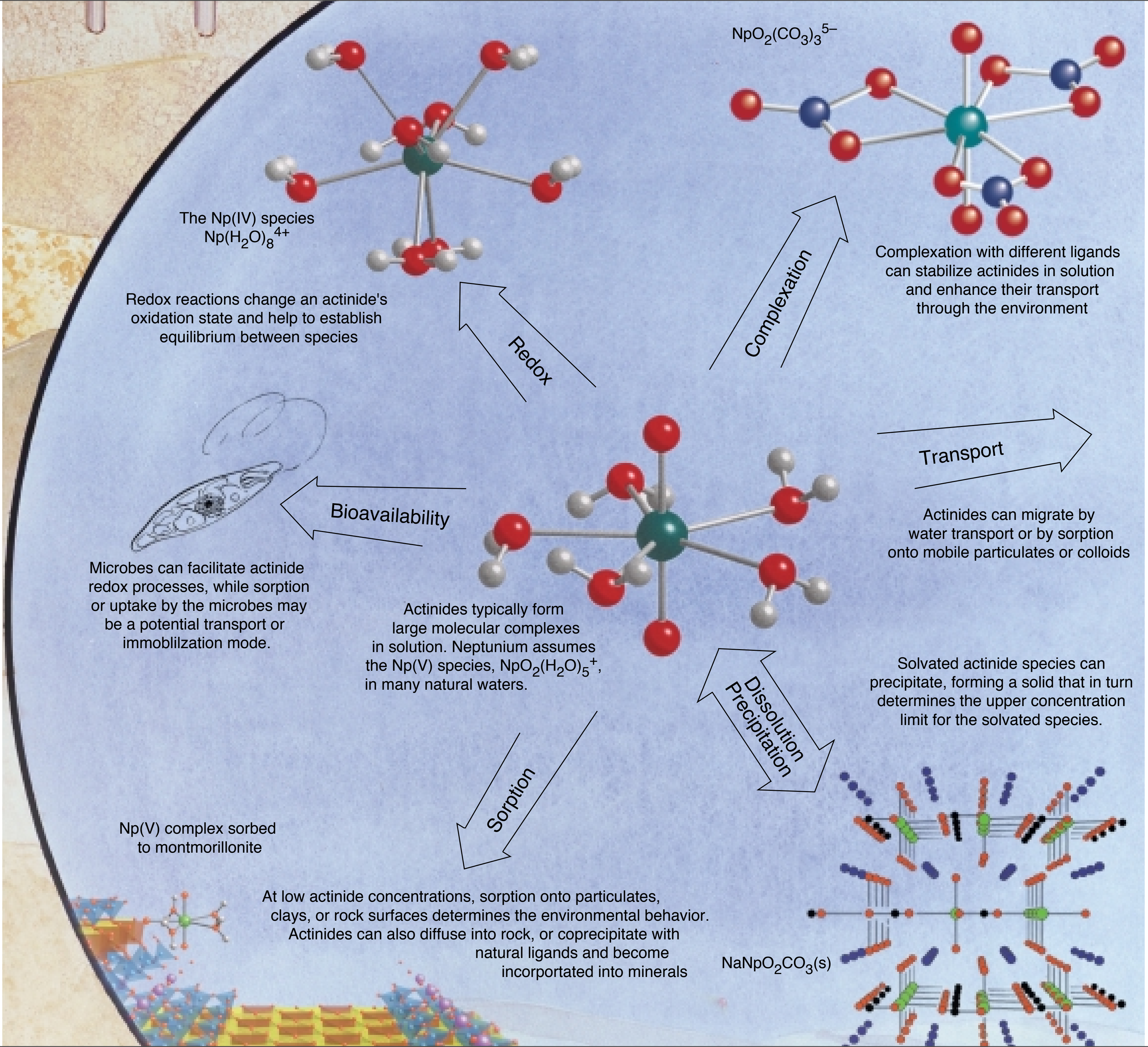
$$\mathrm{An}^{4+}(\mathrm{IV}) > \mathrm{An}^{3+}(\mathrm{III}) \approx \mathrm{AnO}_2^{2+}(\mathrm{VI}) > \mathrm{AnO}_2^{+}(\mathrm{V})$$

More Oxidizing Environment



$$\mathrm{O}_2 + 4\ \mathrm{H}^+ + 4\ \mathrm{e}^- \rightarrow 2\ \mathrm{H}_2\mathrm{O} \quad 1.23\ \mathrm{V}$$

$$2\ \mathrm{H}_2\mathrm{O} + 2\ \mathrm{e}^- \rightarrow \mathrm{H}_2 + 2\ \mathrm{OH}^- \quad -0.83\ \mathrm{V}$$



The Np(IV) species
$Np(H_2O)_8^{4+}$

Redox reactions change an actinide's oxidation state and help to establish equilibrium between species

Redox

Complexation

$NpO_2(CO_3)_3^{5-}$

Complexation with different ligands can stabilize actinides in solution and enhance their transport through the environment

Transport

Actinides can migrate by water transport or by sorption onto mobile particulates or colloids

Bioavailability

Microbes can facilitate actinide redox processes, while sorption or uptake by the microbes may be a potential transport or immoblilzation mode.

Actinides typically form large molecular complexes in solution. Neptunium assumes the Np(V) species, $NpO_2(H_2O)_5^{+}$, in many natural waters.

Dissolution
Precipitation

Solvated actinide species can precipitate, forming a solid that in turn determines the upper concentration limit for the solvated species.

Sorption

Np(V) complex sorbed to montmorillonite

At low actinide concentrations, sorption onto particulates, clays, or rock surfaces determines the environmental behavior. Actinides can also diffuse into rock, or coprecipitate with natural ligands and become incorportated into minerals

$NaNpO_2CO_3(s)$

Conclusions & Open Questions

- Relativistic DFT calculations of aqueous actinides have been carried out.
- Evidence of strong correlations.
- Can better quantitative agreement be achieved?
- Will the same approach explain neptunium and americium?
- Organizing principle at work?
- Application to complexation with carbonates, etc.?