Relativistic equation of motion coupled cluster theory (based on four-component Hamiltonians)

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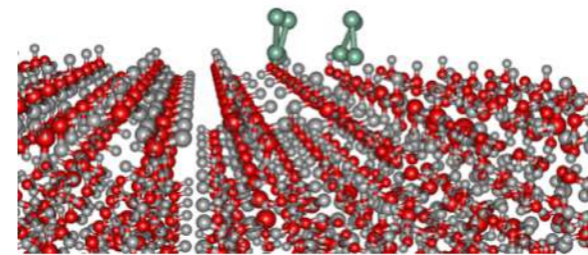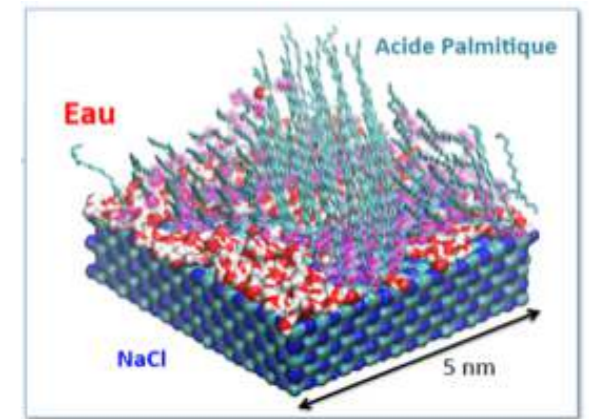http://phlam.univ-lille.fr

Aerosols

- Atmospheric chemistry and physics

  - (reactive) processes over e.g. ice surfaces (polar clouds)

  - Industrial accidents : release of fission products in the environment (Re, Pu, I, …)
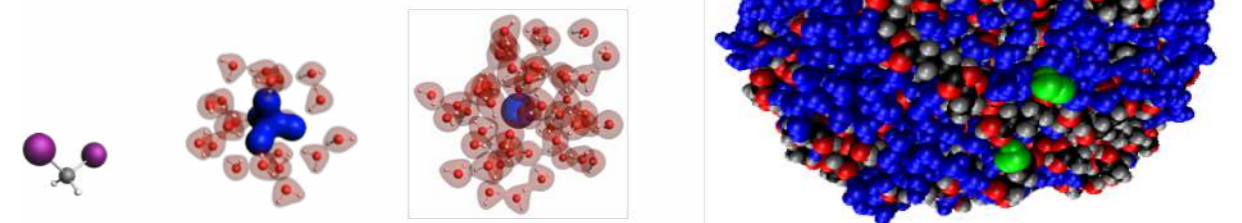
    - transport through the atmosphere

Halogens

ice particles

marine aerosols

- Microscopic to nanoscopic description

- molecular properties = speciation !

microscopic

nanoscopic

Electronic states with 4-component coupled cluster

- Intermediate Hamiltonian Fock-space (IHFSCC) method (**DIRAC code**) [1]

  - Single/double attachment (EA/DEA), detachment (IP/DIP), excited states (EE)

  $$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle \quad \longrightarrow \quad \hat{H}_{\mathrm{eff}}|\varphi_m\rangle = \Omega^{-1}\hat{H}\hat{\Omega}|\varphi_m\rangle = E_m|\varphi_m\rangle$$

  $$|\Psi_k\rangle = \hat{\Omega}|\varphi_k\rangle \qquad \hat{\Omega} = \exp(\hat{S}) \qquad \hat{S} = \hat{S}^{(0,0)} + \hat{S}^{(1,0)} + \hat{S}^{(0,1)} + \hat{S}^{(1,1)} + \ldots$$

  $$\mathrm{M}(0,0) \to \mathrm{M}^+(1,0) \to \mathrm{M}^-(0,1) \to \mathrm{M}^{(*)}(1,1)$$

  - intruder states: IH formulation ($P = P_m + P_i$) (see [2] for example)

- Equation of motion coupled cluster : EOM-EE/IP/EA (here will exemplify w/ IP)

  $$|\Psi_k\rangle = \hat{C}_k \exp(\hat{T})|\Phi_{\mathrm{HF}}\rangle \qquad \hat{\mathbf{C}}_k^{\mathrm{EOM\text{-}IP}} = \sum_i c_{k;i}\{a_i\} + \sum_{a,m>i} c_{k;im}^a\{a_a^\dagger a_m a_i\} + \ldots$$

  - no model spaces, no intruder states, balanced description of excited states

  - **4C-based EOM-CC implementation** (see for [3] for details)

[1] Visscher, Eliav, Kaldor, JCP 2001, **115**, 9720
[2] Infante, Gomes, Visscher JCP 2006, **125**, 074301
[3] Shee, Saue, Visscher, Gomes, JCP 2018, **149**, 174113
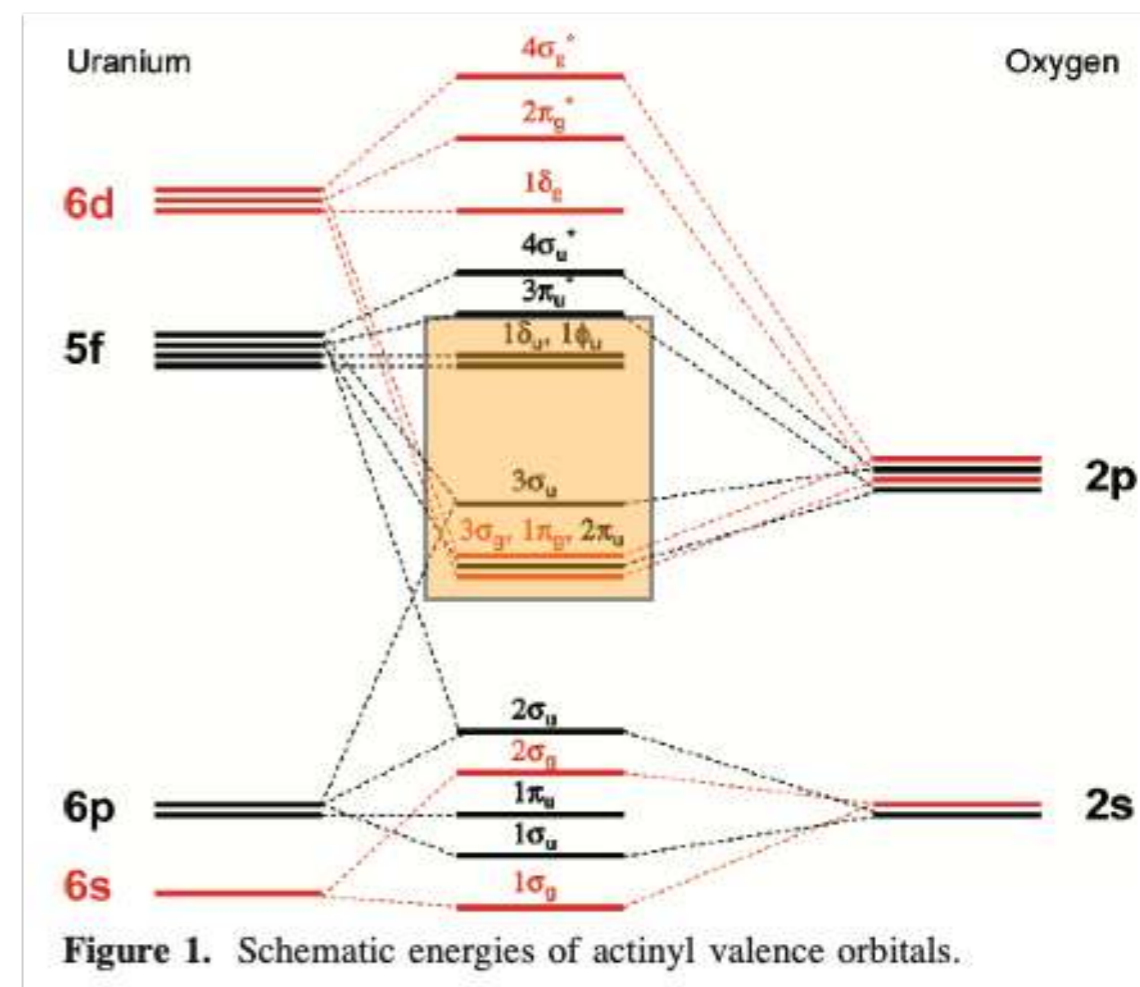
Volatile plutonium oxides

- Major radioprotection concern in the case of solvent fires in reprocessing plants

  - Oxides and oxo-hydroxides (PuO_2, $PuO_2(OH)_2$, PuO_3)

- Estimation of species formed requires accurate thermochemical data

  - Many experimental PuO_2 $\Delta_f H^\ominus$(298.15K), but few for $PuO_2(OH)_2$ and PuO_3

- Theoretical determination of $\Delta_f H^\ominus$(298.15K) and $C^\ominus_P(T)$ [1] and thermodynamic equilibrium calculations (MEPHISTA/IRSN)

  - $^2DC^M$ CCSD(T)/CBS enthalpies of formation for PuO_2 (-449±7 kJ/mol) in good agreement to experiment (-440±7 kJ/mol)

  - SO-CASPT2/CBS calculations for $PuO_2(OH)_2$, PuO_3 (strong multireference character [2]) and PuO_2 in good agreement with experiment (large error bars)

  - Extremely poor performance of B3LYP for all species

[1] Kervazo *et al*, IC 2019, **58**, 14507
[2] Boguslawski *et al*, PCCP 2017, **19**, 4317

Volatile plutonium oxides: ionized states of PuO$_2$

- Large variation of experimental values, depending on measurement technique

- Adiabatic ^{2}DC^M EOM-IP-CCSD/CBS ionization energies

  - Ionization from non-bonding ($\delta_{3/2u}$, $\varphi_{5/2u}$) and bonding ($\sigma_{1/2u}$, $\pi_{3/2u}$) spinors

  - Experiments seem to probe excited ionized states

Figure 1. Schematic energies of actinyl valence orbitals.

Denning JPCA 2007, **111**, 4125

Ω	R$_{eq}$/Å	EOM-IP[1]/eV	Exp[2]/eV	Exp[3]/eV	Exp[4]/eV	Exp[5]/eV
3/2u	1.697	7.07	6.6			
5/2u	1.688	7.20		7.03±0.12		
1/2u	1.771	9.37			9.4±0.5	
3/2u	1.831	10.79				10.1±0.1

[1] Kervazo *et al*, IC 2019, **58**, 14507; [2] Gibson *et al*, JPCA 2006, **110**, 4131; Capone *et al* JPCA 2006, **109**, 12054; [3] Santos *et al*, JPCA 2002, **106**, 7190; [4] Capone *et al*, JPCA 1999, **103**, 10899; [5] Rauh and Ackerman, JCP 1974, **60**, 1396

Electron binding energies of solvated halides

- Electron binding energies (BEs) provide information on the organization of the solvated species, require the description of the environment

  - Implicit models (PCM) fail to capture (large) solvent shifts [1], state of the art: CPMD simulations, Green's functions calculations based on DFT orbitals [2]

- Frozen density embedding (FDE) [3] (see [4] for details)

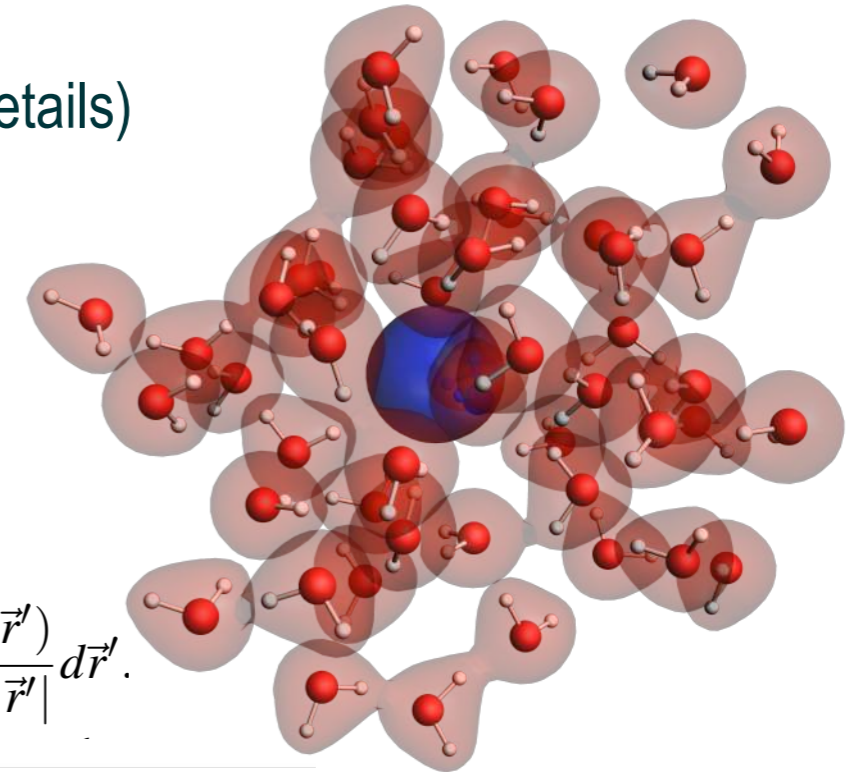$$\rho_k^{tot}(\vec{r}) = \rho_k^I(\vec{r}) + \rho_k^{II}(\vec{r})$$

$$E_{tot}[\rho_k^{tot}] = E_I[\rho_k^I] + E_{II}[\rho_k^{II}] + E_{int}[\rho_k^I, \rho_k^{II}]$$

  - KS-like equations with embedding potential

$$v_{emb;k}^I(\vec{r}) = \frac{\delta E_{int}}{\delta \rho_k^I(\vec{r})} = \frac{\delta E_{xc}^{nadd}}{\delta \rho_k^I} + \frac{\delta T_s^{nadd}}{\delta \rho_k^I} + v_{nuc}^{II}(\vec{r}) + \int \frac{\rho_0^{II}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'.$$

$$X^{nadd} \equiv X^{nadd}[\rho_k^I, \rho_k^{II}] = X[\rho_k^{tot}] - X[\rho_k^I] - X[\rho_k^{II}]$$

- Simple CC-in-DFT scheme [5]

[1] Winter *et al.*, JACS 2005, **127**, 7203
[2] Gaiduk *et al.*, JACS 2016, **138**, 6912
[3] Wesolowski PRA 2008, **77**, 012504
[4] ASP Gomes, CR Jacob, Annu. Rep. Prog. Chem. Sect. C: Phys. Chem. 2012, 108, 222
[5] Gomes, Jacob, Visscher, PCCP 2008, 10, 5353

Simulating halides in water droplets

- Classical MD with polarizable FFs **(Polaris(MD))** (M Masella CEA/DSV) for X⁻ / water droplet, 200 snapshots

- Water: SR-ZORA Hamiltonian, SAOP (TZ2P) **(ADF)**

- X⁻ with SAOP [1], EOM-IP-CCSD with DC Hamiltonian (t-aug Dyall nZ for X, Dunning cc-pVnZ for H, O)

- Embedding (**PyADF**): PW91k, PBE nadd xck, BEs averaged over 200 (SR-ZORA) or 100 (4C) snapshots

- SAOP model potential [1] (~GGA cost)

  - enforce proper asymptotic behavior for XC potential

$$\epsilon_N = -I_p$$

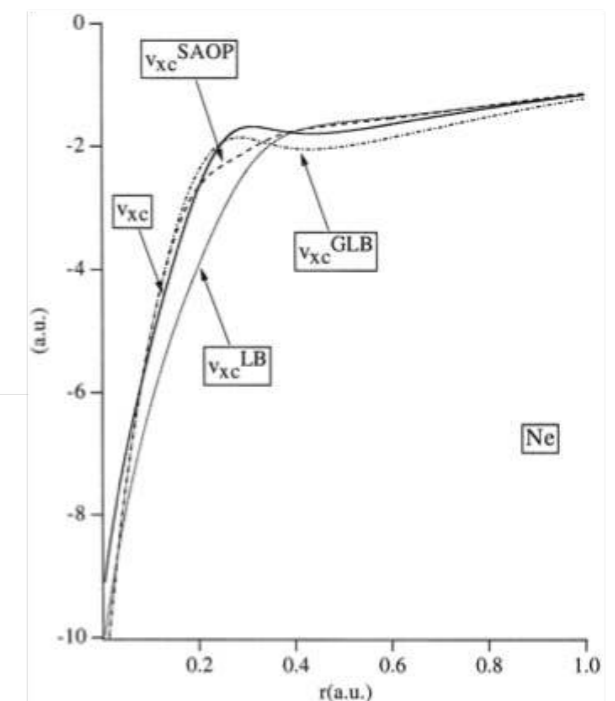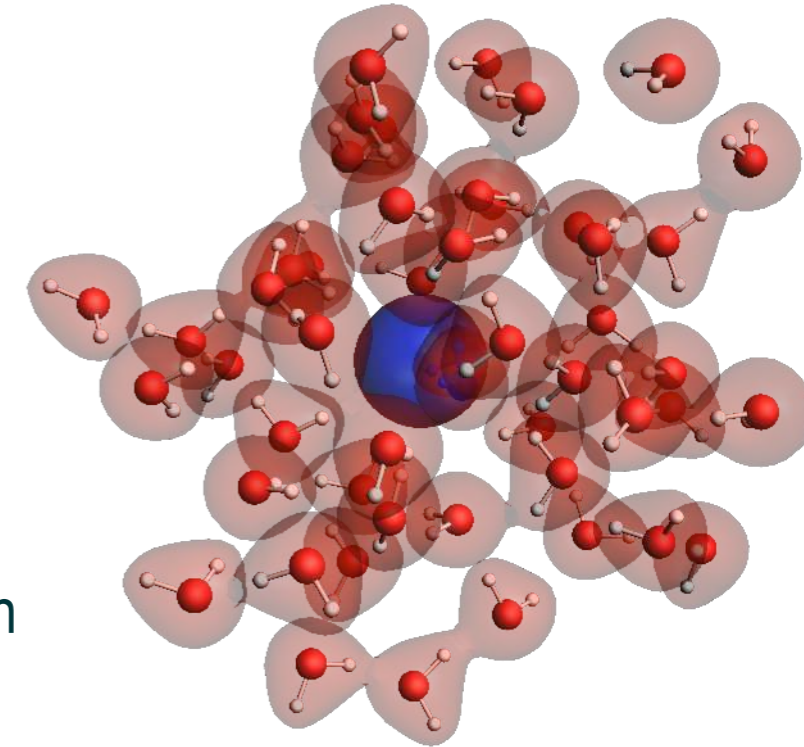[1] Gritsenko, Schipper, Baerends, CPL 1999, **302**, 199

Fig. 3. Comparison of the accurate exchange-correlation potential for Ne with the LB, GLB and SAOP potentials.

Calculating electron binding energies : gas-phase

- SAOP underestimates EOM-IP-CCSD BEs by ~0.1-0.4 eV

- EOM-IP-CCSD overestimates experimental BEs by ~0.1 eV

Species	state	SAOP / eV		EOM-IP-CCSD / eV		Exp. / eV
		TZ	CBS	TZ	CBS	
F⁻	$^2P_{3/2}$	3.16	3.16	3.32	3.45	3.40 [1, 2]
Cl⁻	$^2P_{3/2}$	3.41	3.41	3.59	3.77	3.62 [3, 4]
Br⁻	$^2P_{3/2}$	3.23	3.23	3.40	3.48	3.37 [5, 6]
I⁻	$^2P_{3/2}$	3.02	3.02	3.21	3.19	3.06 [7]
At⁻	$^2P_{3/2}$	2.48	2.48	2.41	2.55	2.40 [8]
H_2O	b_1	12.33				12.62 [9]

[1] Popp, Z. Naturforsch. 1967, **22A**, 254

[2] Milstein and Berry, JCP 1971, **55**, 4146

[3] Mück and Popp, Z. Naturforsch. 1968, **23A**, 1213

[4] McDermid and Webster, J. Phys. (Paris), Colloq. 1983, **44**, C7-461

[5] Berry and Reimann, JCP 1963, **38**, 1540

[6] Frank, Neiger, Popp, Z. Naturforsch. 1970, **25A**, 1617

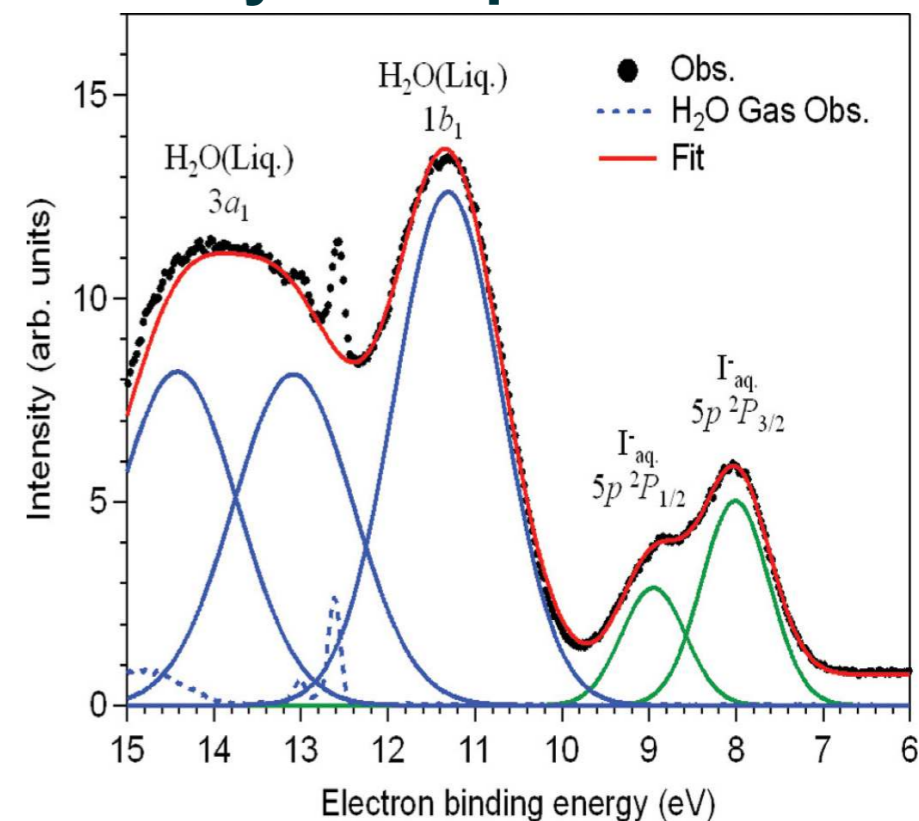[7] Webster, McDermid, Rettner, JCP 1983, **78**, 646

[8] Borschevsky et al., PRA 2015, **91**, 020501

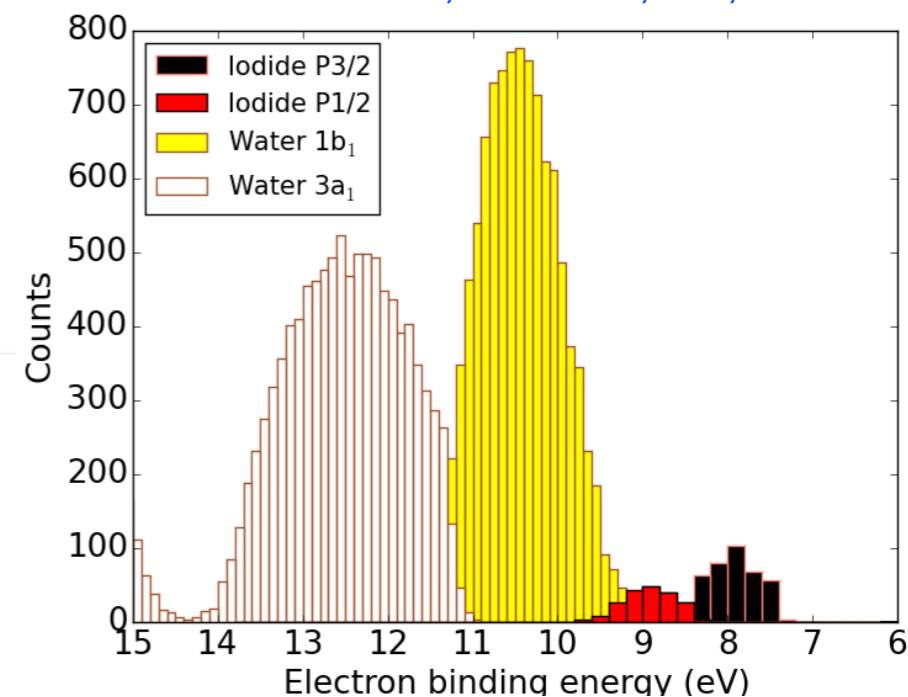[9] Reutt, Wang, Lee, Shirley, JCP 1886, **85**, 6928

Calculating electron binding energies : Theory vs Experiment

- Comparisons for iodide

  - EOM-IP-CCSD

    - absolute energy differences and $^2P_{3/2}$ - $^2P_{1/2}$ separation are quite good

  - SAOP

    - Systematic underestimation (~1 eV) of water bands: droplet size effects

State	Experiment / eV	Theory / eV
$^2P_{3/2}$	8.03(6)	8.0(3)
$^2P_{1/2}$	8.96(7)	9.0(3)
b_1	11.31(4)	10.4(5)
a_1	13.78(7)	12.5(4)

Kurahashi *et al.*, JCP 2014, **140**, 174506

Bouchafra *et al.*, PRL 2018, **121**, 266001

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Calculating Cl⁻ BEs : comparison of methods

Method	BE (Cl⁻) / eV
G_0W_0/PBE [1]	8.76
G_0W_0/PBE0 [1]	9.43
G_0W_0/RSH [1]	9.86
G_0W_0/sc-hybrid [1]	9.89
OVGF/PCM [2]	10.53
P3/PCM [2]	10.32
P3/$[X(H_2O)_6]^-$ [3]	6.95
P3/$[X(H_2O)_6]^- + (H_2O)_{60}$ (PC) [3]	9.41
SAOP-in-SAOP [4]	$^2P_{3/2}$: 9.4; $^2P_{1/2}$: 9.5
EOM-IP-CCSD-in-SAOP [4]	$^2P_{3/2}$: 9.9; $^2P_{1/2}$: 10.1
Exp. [5]	9.60(7)
Exp. [6]	9.5(2)

- G_0W_0 results quite sensitive to underlying orbitals

- PCM inadequate

- FDE-based approaches

  - consistent with PC model

  - SAOP-in-SAOP competitive with G_0W_0, but at lower cost

  - EOM-IP similar to G_0W_0/sc-hybrid, slight overestimation

[1] Gaiduk *et al.*, JACS 2016, **138**, 6912
[2] Dolgounitcheva *et al.*, IJQC 2012, **112**, 3840
[3] Canuto *et al.*, JCP 2010, **132**, 214507
[4] Bouchafra *et al.*, PRL 2018, **121**, 266001
[5] Winter *et al.*, JACS 2005, **127**, 7203
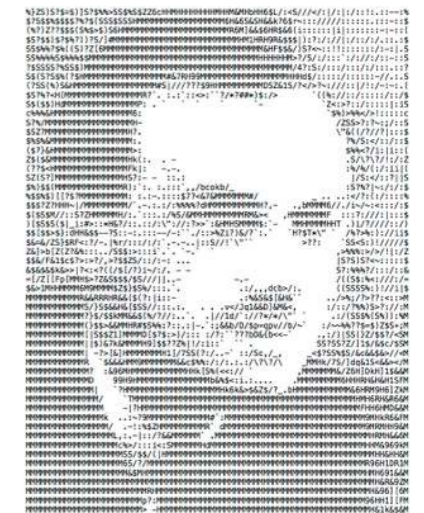[6] Kurahashi *et al.*, JCP 2014, **140**, 174506

Concluding remarks

- Relativistic EOM-IP/EE/EA-CCSD code exploiting point-group symmetry in DIRAC

  - Black-box alternative to (IH)FSCCSD

  - easily explore Hamiltonians ($^2DC^M$, DC,…)

- New insight into low-lying ionized states of PuO_2

  - Discrepant experimental IEs : different ionized electronic states

- Environment effects on BEs across the periodic table

  - QM description of all species (EOM-IP-CCSD-in-DFT)

  - Size effects important for water droplet BEs

    - Impurity models [1] could be explored for BEs in bulk water

[1] Tölle *et al*, IJQC 2019, e25801

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