COMMUNICATION

Relativity and the mercury battery

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5 **Comparative, fully relativistic (FR), scalar relativistic (SR) and non-relativistic (NR) DFT calculations attribute about 30% of the mercury-battery voltage to relativity. The obtained percentage is smaller than for the lead-acid battery, but not negligible.**

10 Relativistic effects can strongly influence the chemical properties of heavier elements. A striking example was found in the recent study of the cell reaction of the common lead-acid battery.[1] We could well reproduce its standard voltage of 2.107 V by the calculations on the three solids involved. Furthermore, over 1.7 V 15 or 80% of this electromotoric force (EMF), E^O, arise from relativistic effects. As stated, 'cars start due to relativity'.

How about other batteries? An obvious example, containing a heavy element, is the previously common mercury battery[2], 20 whose two-electron cell reaction[3] is:

$$Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l), \qquad E^O = +1.35 \text{ V.} \quad (1)$$
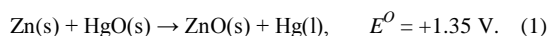
Here, Hg is a liquid, while ZnO, Zn and HgO are solids.[4] 25 Qualitatively, we could estimate the magnitude of the relativistic effects by claiming that Cd is non-relativistic (NR) mercury. The experimental data[3, 7] then gives:

$$Zn(s) + CdO(s) \rightarrow ZnO(s) + Cd(s), \qquad E^O = +0.47 \text{ V.} \quad (2)$$
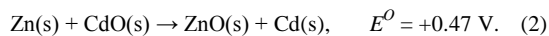
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Assuming for a moment that Cd ≈ Hg(NR) and CdO ≈ HgO(NR) and based on the experimental values of the EMF of reactions (1) and (2) one can estimate that up to +0.88 V or 65% of $E^O(1)$ comes from relativity[5]. Obviously Cd is not Hg, either relativistic 35 or not, and there are other factors that may affect the final relativistic contributions to EMF.[6]

Let us come back on the reaction (1). Indeed, the experimental cell thermodynamics are well known[7], but here we approach them 40 from an *ab-initio* point of view. Our goal is to investigate the relativistic effects on the E^O of the cell, which we derive from the cell free energy of the reaction (1), ΔG^O, using

$$\Delta G^O = -n \cdot F \cdot E^O, \qquad (3)$$

45 giving

$$E^O = -\Delta G^O / n \cdot F. \qquad (4)$$

50 Here $n=2$ is the number of electrons transferred and F is the Faraday constant.

Earlier calculations were reported on the MO (M=Zn, Hg) oxides by Glanss *et al.*[8] and Biering *et al.*[9] and on the metals M by 55 Gaston *et al.*[10, 11, 12], Wedig *et al.*[13] and by Moriarty.[14] Gaston *et al.* find that the cohesion of solid Hg requires both three-body correlation and relativistic effects.[11] For the cohesive energy using the incremental method see also the work of B. Paulus *et al.*[15] Biering *et al.* found that at the non-relativistic level HgO 60 spontaneously relaxes to form a rock salt structure, thus already the very structure of HgO originates from the inclusion of relativity; in this particular case, from the scalar effects.[9]

Here, we consider the electronic relativistic effects through the 65 means of density functional theory (DFT) coupled with the zeroth-order regular approximation (ZORA). We neglect structural changes due to relativity, thus capturing the dynamic electronic effects of relativity only.

70 **Methodology**: The prediction of formation energies in a quantitative manner from *ab-initio* calculations requires, in

Table 1. Comparison of the experimental and calculated electromotoric force, E^O, of the mercury-battery reaction (1). 75 Level of relativity: NR – Non-relativistic, SR – Scalar relativistic, FR – Fully-relativistic.

Method		E^O [V]			ΔE^O [V]		
		NR	SR	FR	(FR-NR)	(SR-NR)	(FR-SR)
VASP	PBE	---	+1.04	+1.04	---	---	+0.00
	PBE[a]	---	+1.15	+1.13	---	---	-0.02
BAND	LDA	+0.70	+1.10	+1.10	+0.40	+0.40	+0.00
	PBE	+0.62	+1.02	+1.02	+0.40	+0.40	+0.00
	PBE-D	+1.03	+1.43	+1.43	+0.40	+0.40	+0.00
	PBEsol	+0.66	+1.04	+1.05	+0.38	+0.38	+0.00
	PBEsol-D	+0.93	+1.31	+1.31	+0.38	+0.38	+0.00
	Exp. [7]	---	---	+1.346[b]			
	Exp. [2]	---	---	+1.358[c]			

[a] Structures relaxed [b] Standard conditions [c] Standard conditions but with Hg heat of fusion included

Table 2. Heats of formation, ΔH, calculated with respect to spherically symmetrical atoms at different levels of relativity [BAND/PBEsol-D/TZ2P, 0K].

Level of relativity	ΔH [V/f.u.][a]			
	Zn(s)	ZnO(s)	Hg(s)	HgO(s)
FR	-1.75	-9.62	-1.89	-7.14
SR	-1.75	-9.62	-1.79	-7.04
NR	-1.84	-9.87	-2.39	-8.45
Δ(FR-SR)	+0.00	+0.00	-0.11	-0.10
Δ(SR-NR)	+0.10	+0.25	+0.61	+1.52
Δ(FR-NR)	+0.10	+0.25	+0.50	+1.42

[a] f.u. = formula unit

addition to having an accurate underlying theory, also good convergence of all technical parameters including a sufficiently large basis set. It is therefore meaningful to approach the problem with several independent methods, and see if they converge on the result. In our case, we used a linear combination of local orbitals, with and without a frozen-core approximation, using the BAND program[16], and a plane-wave based program VASP.[17, 18, 19] With BAND we employed the following exchange-correlation functionals: SVWN,[20] PBE,[21] PBEsol,[22] and also PBE-D and PBEsol-D alternatives, where the two last ones include dispersion corrections[23, 24]. For VASP we used the PBE functional only.

We investigate the relativistic effects using the BAND program by means of the zeroth-order regular approximation (ZORA, see Ref. [25] and references therein). We consider three cases: non-relativistic (NR) with no ZORA operators, scalar relativistic (SR) including ZORA but without the spin-orbit coupling part, and the fully relativistic (FR) case with complete ZORA where first-order spin-orbit effects are also taken into account. To ensure high-accuracy results, the convergence of the calculations was checked with respect to all crucial numerical parameters including the number of **k**-points, the basis-set quality, and the size of the frozen core.

In the BAND calculations we apply Slater-type triple-zeta basis sets augmented with two polarization functions, taken from the BAND basis-set repository. The frozen-core approximation is applied to reduce the size of the variational basis set. The use of frozen core, as implemented in BAND[16], is preferable over pseudo-potentials because it essentially allows for all-electron calculations. The frozen-core orbitals are taken from high-accuracy calculations with extensive Slater-type orbital basis sets. For oxygen, we use all-electron basis sets. For zinc we include up to 3p and for mercury up to 4f orbitals in the core.

The calculations are performed for experimental crystal structures (given as supplementary material), allowing no structural relaxations. Thus we capture the dynamic electronic effects of relativity (meaning Dirac versus Schrödinger). While in our BAND calculations the lattice constants and atomic positions were kept fixed, we did consider relaxation effects in our VASP

calculations. At scalar and fully relativistic levels we found relaxation effects to have minor effect on the E^O (see Table 1).

Because solids are easier to handle theoretically and because we perform our calculation at 0K, we use solid rather than liquid Hg throughout the calculations.[26] The thermal effects on the reaction energies are small and are neglected[27] as are the zero-point vibrational contributions to the energy. If the battery freezes at low temperatures, it is due to the kinetics and not due to significantly different $\Delta G(1)$ at 0K. In the actual calculation of the EMF of reaction (1) we thus effectively use $\Delta G^O \approx \Delta G(0K) = \Delta H(0K)$.

Discussion: In case of the lead battery we had a single, dominant source for the relativistic effect, *viz.* the relativistic stabilization of the Pb 6s shell, which made the Pb(IV)O$_2$ reactant a high-energy species. An unexpected, smaller contribution came from a relativistic stabilization of the PbSO$_4$ product of the discharge reaction.

How about the present reaction (1)? We see from Table 2 that the same relativistic 6s stabilization raises the energy of the HgO reactant. The density of states (DOS) of HgO shows significant hybridization between the Hg 6s and 5d shells with the O 2p shell.[8, 9] This effect is expected to lower the relativistic stabilization of HgO. Indeed, in our DFT model the stabilization of HgO is calculated to be smaller than that of PbO$_2$ by about half of that amount. In the case of mercury, the 6s shell is full, and the binding energy is also diminished. Thus, HgO goes up but also Hg goes up. Similar effects, though smaller, are observed for Zn and ZnO (see Table 2). This effectively diminishes the total relativistic effect on $E^O(1)$.

Because valence-shell relativistic effects roughly scale, down a column[28], as Z^2, the ratio of the analogous effects on Zn and Hg, and their oxides, is expected to be

$$\left[\frac{Z(Zn)}{Z(Hg)}\right]^2 = \left[\frac{30}{80}\right]^2 = 0.14. \qquad (5)$$

Indeed, the ratio of the relativistic shifts, Δ(FR-NR), is for Zn(s)/Hg(s), +0.10/+0.50 = 0.20 and for ZnO(s)/HgO(s) +0.25/+1.42 = 0.18.

Conclusions

The dominant uncertainty in our model arises mainly from the metals, whose cohesive properties already contain substantial dispersion. These effects have been recently invoked to explain the large *c/a* ratios of Zn and Cd[9, 29] and the rhombohedral structure of Hg[8]. Interestingly, the signs for large *c/a* ratio can already be seen in the tetrahedral M_n clusters, M=Zn, Cd; n = 35, 56.[30] The correlation effects are also of importance. Paulus and Rosciszewski pointed out that Hg is not bound at the Hartree-Fock level of theory, and thus all the binding comes from electron correlation.[31]

Methodologically one source of uncertainty is the DFT itself which is inherently unable to reliably reproduce the dispersion interactions. By replacing the pure DFT, PBE and PBEsol

functionals with their dispersion-corrected analogues the reproduction of the EMF is significantly improved. The best agreement with experiment is obtained by applying the PBEsol-D functional. Compared to the experimental cell voltage of +1.35 V our relativistic best estimate yields +1.31 V.

Our key result is that about +0.38 V or 29% of the calculated +1.31 V of the mercury battery's EMF arise from relativistic effects. Like in the case of the lead-acid battery[1], the largest relativistic contribution comes from the destabilization of a reactant heavy-metal oxide, HgO(s), where 6s electrons are formally removed. Scalar relativistic effects dominate. The small spin-orbit effects come from Hg(s) and HgO(s) but cancel for the full reaction.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: [Structures used to simulate Hg(s), HgO(s), Zn(s) and ZnO(s).]. See DOI: 10.1039/b000000x/

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2 The mercury battery has been first patented by C. L. Clarke in 1884 (US Patent 298175). It became widely used in the 1940s when Samuel Ruben developed a balanced mercury cell used for military applications. The batteries become highly popular during the World War II due to their large storage capacity, long shelf life (up to 10 years) and stable voltage output. After the WW II it has been widely applied in small electronic devices including: pacemakers, hearing aids, calculators, radios and other portable electronic apparatus. The battery lost its importance once the ban on mercury-containing products has been enforced in the 1990s.

3 Standard conditions: 293.15 K, 101.325 kPa.

4 Actually the zinc is in form of an amalgam. We neglect the difference.

5 Here, we assume the following: Cd(FR,s) ≈ Hg(NR,s) and CdO(FR,s) ≈ HgO(NR,s). Then the difference $\Delta E = E^O(1) - E^O(2) = +0.88$ V corresponds to the relativistic contribution of the total EMF of the reaction (1).

6 Note for instance that Cd and CdO adopt structures different than Hg and HgO, respectively.

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27 At standard conditions: $\Delta C^O_p(1) = -1.23$ J·K^{-1}·mol^{-1} and $\Delta S^O(1) = +7.74$ J·K^{-1}·mol^{-1}]. Assuming, in the first approximation, constant heat capacities, the thermal correction to E^O is $\int_0^{293.15} dT \Delta C^O_p(1) = -0.003$ eV. We note that although this is only a rough estimate, the actual magnitude of the error should not exceed it.

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