Data-Enabled Computational Chemistry to Better Understand Water Quality

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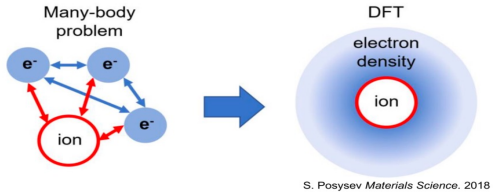
UMBC

Statement of the Problem

Lead release in water systems can cause devastating effects in communities. We need to better understand the atomistic processes that lead to protective thin film formation or lead release. The tool that we can use to do this is first principles density functional theory. It yields atomistic information on the solid state and its electronic structure. This tool can be used to better understand processes that occur in vacuum or in an aqueous environment, but will be even better if we add in real world data to approach real world conditions.



$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_{\text{H}}[\rho](\vec{r}) + V_{\text{xc}}(\vec{r})\right)\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r}).$$

P. Hohenberg and W. Kohn, Phys. Rev. ***136****, B864 (1964)*
W. Kohn and L. J. Sham, Phys. Rev. ***140****, A1133 (1965)*

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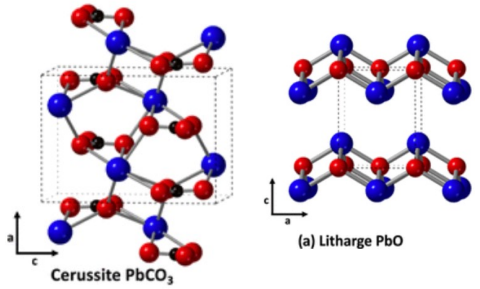
What is Density Functional Theory?

(DFT) is a quantum-mechanical method used in chemistry and physics to calculate the electronic structure of atoms, molecules and solids. It simplifies the problem of having many ions interacting at once by removing exchange and correlation and creating 1-electron states in an external electric field. DFT calculations also take place at absolute zero and in vacuum. This means that a) temperature and pressure and b) exchange and correlation needed to be added back into DFT results to approximate experiments at standard conditions.

Methodology

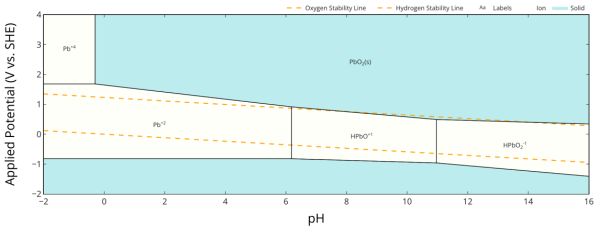
ICSD
FIZ Karlsruhe – Leibniz Institute for Information Infrastructure

- The ICSD has over 280,000 crystal structures.
- 80% of the crystals are classified in a structure type and there are roughly 9,000 different structure types.
- We need to search for the structure type that is appropriate to our problem and any related structures with similar chemistry. (PbO, PbCO3, PbHPO4, etc.)
- These structures are the input for our DFT simulations



QUANTUMESPRESSO

- Quantum ESPRESSO is an open-source software package to do electronic structure calculations based on plane wave DFT, employing pseudopotentials and multiple structure relaxation schemes
- All bulk solids and their surfaces are solved at absolute zero and in vacuum



Data + DFT + More Data

- The input of our DFT is structural data that comes from crystallographic structural databases.
- The output of DFT calculations are electronic states, fully relaxed structures, and total energies.
- Total energy is ΔE or in terms of thermodynamics, a change in internal energy Δ*U*.
- Δ*U* to Δ*G:* add a zero-point energy correction to obtain the DFT piece, $\Delta G_1 = E_{products} - E_{reactants} + ZPE - T\Delta S$
- ΔG_1 : The computable DFT piece that is bond making and bond breaking.
- $\Delta G_2 = \Delta G_{SHE}^0 - n_e e U_{SHE} - 2.303 n_H^+ kT\ \text{pH} + kT \ln a(H_x AO_y)$ is the tabulated data with Nernstian corrections. This was informed by experimental data (Pourbaix diagram).
- - Add them together, $(\Delta G_1 + \Delta G_2)$

References/Citations

Surface Transformations of Lead Oxides and Carbonates Using First-Principles and Thermodynamics Calculations
Ryan T. Grimes, Joshua A. Leginze, Robert Zochowski, and Joseph W. Bennett *Inorganic Chemistry* **2021** *60* (2), 1228-1240 DOI: 10.1021/acs.inorgchem.0c03398

materialsproject.org

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