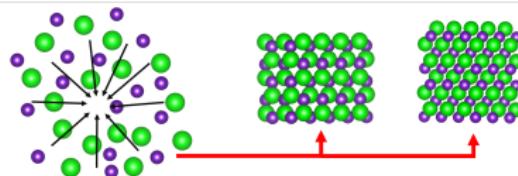
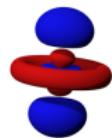


Exploration of Crystal Nucleation Phenomena Through Molecular Simulation

Hayden Scheiber, Patey Group



THE UNIVERSITY OF BRITISH COLUMBIA
DEPARTMENT OF CHEMISTRY



April 29, 2019

Overview

1 Introduction

- Overview
- What is Molecular Dynamics?
- Classical Nucleation Theory
- Our Goal and Questions

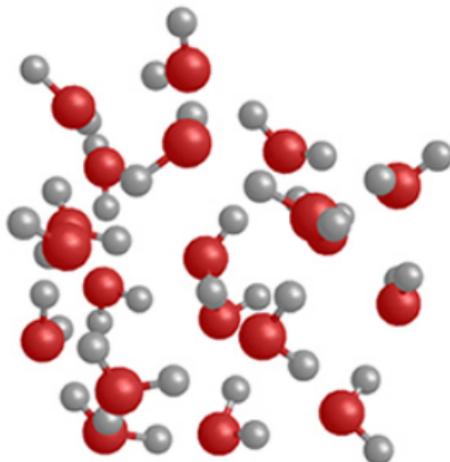
2 My Research

- Solution: Improve the models!
- Ab Initio Calculation Details
- Comparison of Potentials
- Importance of Dispersion

3 Future Work

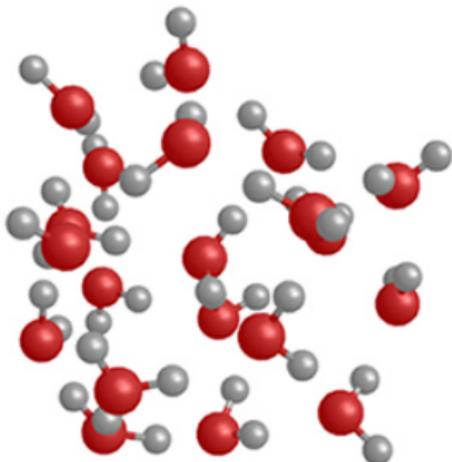
- Nucleation Mechanism of LiX Salts
- Acknowledgments

What is Molecular Dynamics?



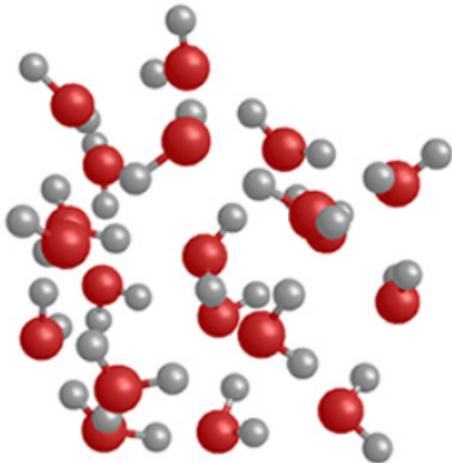
- Molecular Dynamics (MD)
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- Acts as a virtual microscope for **model systems**.

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- Acts as a virtual microscope for **model systems**.
- **Classical MD:** forces are calculated from pre-determined potential energy surface
 - $\vec{F}_i(t, \vec{r}_i) = -\vec{\nabla} u_i(t, \vec{r}_i)$
 - Time is discretized.
(1 - 10 fs)
 - Length Scales: up to 10^7 particles.
 - Time Scales: up to 1 μ s.

Problems with Molecular Dynamics

- Classical MD is **not exact**. Sources of error:
 - Classical equations of motion & empirical potentials.
 - Many-body interactions usually approximated by **effective two-body potentials**.

$$U = \sum_{i=1} \sum_{j>i} u_{ij} + \sum_{i=1} \sum_{j>i} \sum_{k>j} u_{ijk} + \dots \approx \sum_{i=1} \sum_{j>i} u_{ij}^{eff} \quad (1)$$

- Finite-size/cutoff effects.

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- Finite-size/cutoff effects.
- Approximations make MD computationally efficient.
- Allow us to explore larger systems/longer times than **ab initio MD**.
- Models are fit to specific properties, and not strictly **transferable**, but often assumed to be.

Classical Nucleation Theory

Want to improve our understanding of **nucleation theory**.

Currently: **Classical nucleation theory** (CNT)

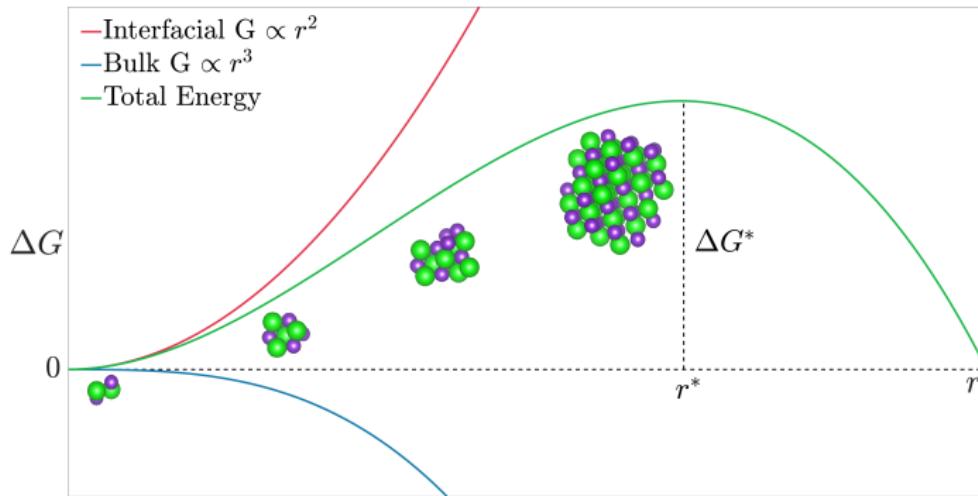
$$\Delta G(r) = \frac{4\pi r^3}{3} \rho \Delta g + 4\pi r^2 \sigma \quad (2)$$

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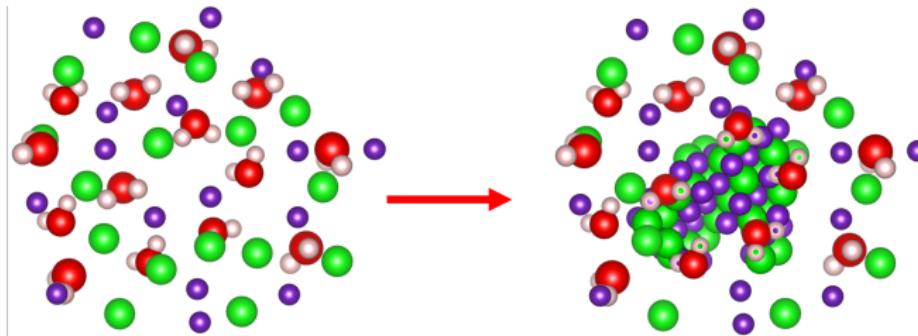
Currently: **Classical nucleation theory** (CNT)

$$\Delta G(r) = \frac{4\pi r^3}{3} \rho \Delta g + 4\pi r^2 \sigma \quad (2)$$



Our Goal

- Assumptions of CNT:
 - Formation of **perfectly spherical clusters**.
 - Nucleation involves a **single free energy barrier**.
 - The interior/surface interactions of nuclei are equivalent to bulk phase interactions.
- Despite these assumptions, CNT is a useful approximation.



Main Questions

I am interested in the cases where CNT is deficient.

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 - Mechanism/theoretical basis not well understood.

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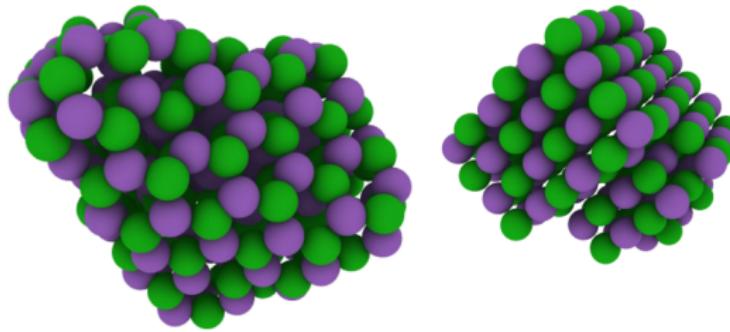
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- The lithium halides present a **simple case study**.
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 - Is this barrier larger than the CNT barrier?
- Structural arrangement (or "**crystallinity**") of nuclei appears to play a critical role in nucleation.
 - Mechanism/theoretical basis not well understood.
- In simulations, LiF does not nucleate at 300 K but does at 500 K. Why?

A big problem

Problem: The available models **usually fail to reproduce the correct crystal structures** of LiX in simulation!

- Additionally, **LiF solubility at 300 K is $\sim 10\times$ too soluble.**
- Two available models: **Tosi-Fumi (TF)** and **Joung-Cheatham (JC).**



TF: Fails for all lithium halides.

JC: Fails for LiBr and LiI only (with SPC/E water).

A big problem

JC Model:

$$u_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

- Coulombic Interaction + Lennard-Jones
- Fit to solvation free energies, RDF's, and lattice parameters, among others.
- Assumed **rocksalt structure!**

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$$u_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

TF Model:

$$u_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + B_{ij} e^{-\alpha_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (4)$$

- Coulombic Interaction + Lennard-Jones
- Fit to solvation free energies, RDF's, and lattice parameters, among others.
- Assumed **rocksalt structure!**

- Coulombic Interaction + Exponential repulsion + dispersion.
- Fit to equation of state and derivatives, lattice energy, and lattice parameters.
- Assumed **rocksalt structure!**

Goals of a model System

- ① Correct ground state **crystal structure**: Rocksalt.
- ② Correct **solubility in water**.

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- ③ Correct experimental **lattice parameters** at 300 K.
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Goals of a model System

- ① Correct ground state **crystal structure**: Rocksalt.
- ② Correct **solubility in water**. Less importantly:
- ③ Correct experimental **lattice parameters** at 300 K.
- ④ Correct experimental **lattice energy**.

Points 3 and 4 are approximately true for JC and TF; points 1 and 2 not!

Side Note

Reported experimental lattice energies were inaccurate (improved).
Experimental solubilities/lattice parameters are very accurate.

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Our calculations were performed using CRYSTAL17.

This is a solid state HF/DFT *ab initio* code which uses Gaussian basis functions.

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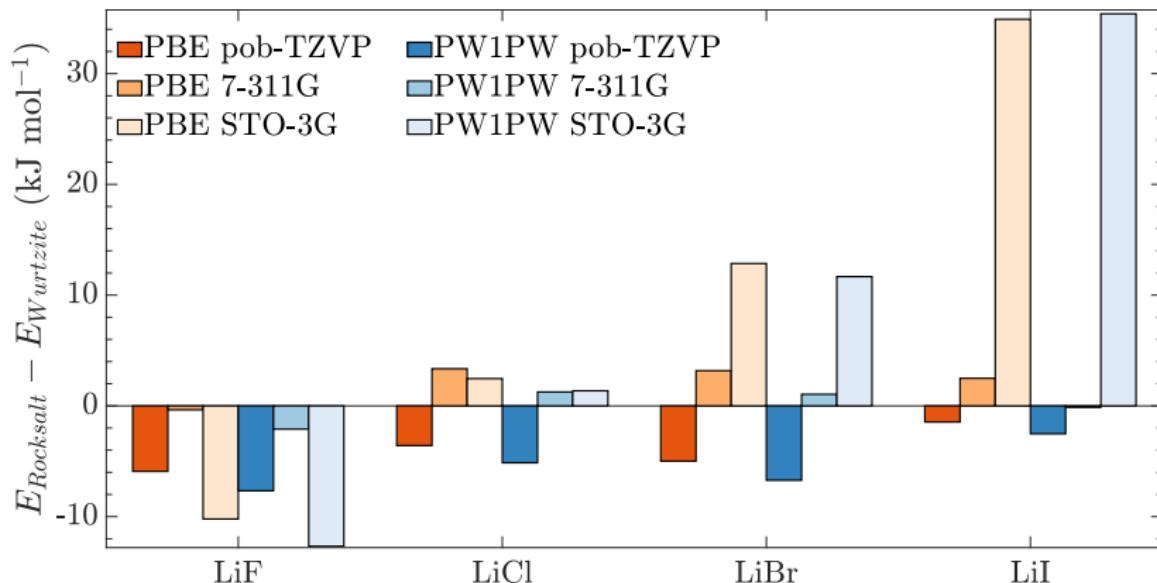
This is a solid state HF/DFT *ab initio* code which uses Gaussian basis functions.

- Crystal atomic orbitals are expanded periodically as **Bloch functions**.
- Recently (2013/2018) released “**pob-TZVP**” basis set is highest quality available for periodic calculations.
- Based on “**def2-TZVP**” basis sets developed for molecules.
- Optimized variationally for solid state. Training sets included **LiX in rocksalt structure**.
- Our study tested wide range of DFT exchange-correlation (XC) functionals.

Most Important Choice: Basis Set

From Experience:

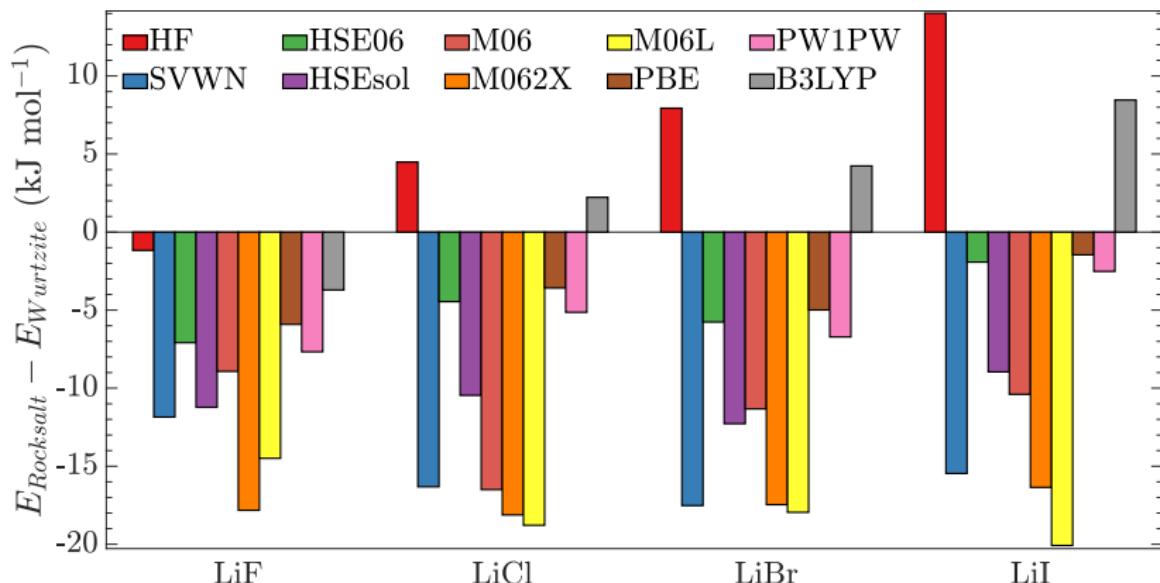
In solid state DFT, choice of Basis set is extremely important.



Less Important Choice: XC Functional

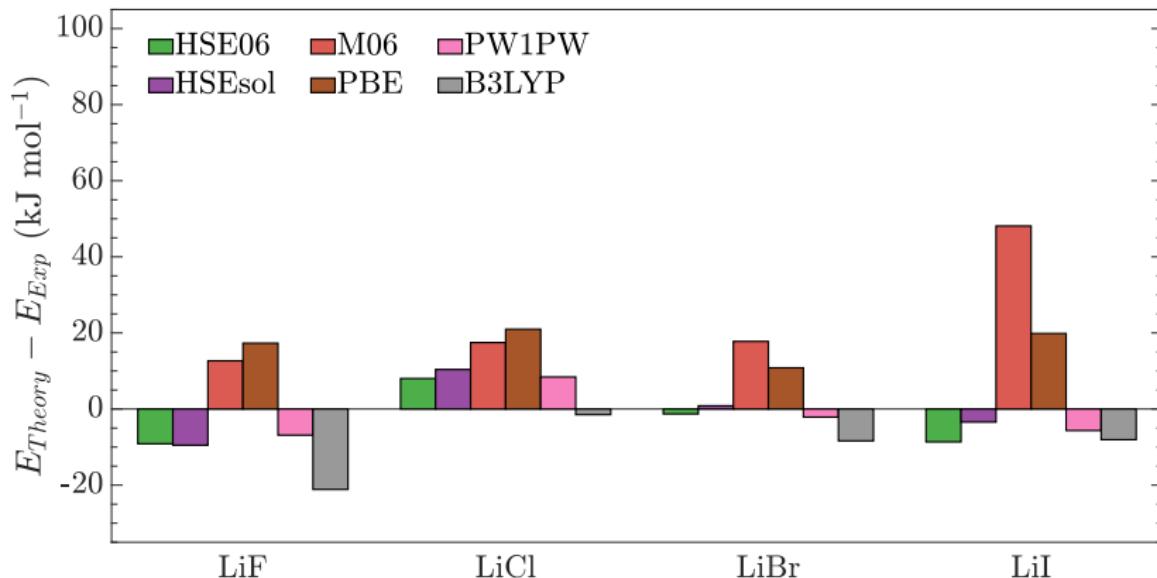
From Experience:

For solid state DFT, the XC is less important.



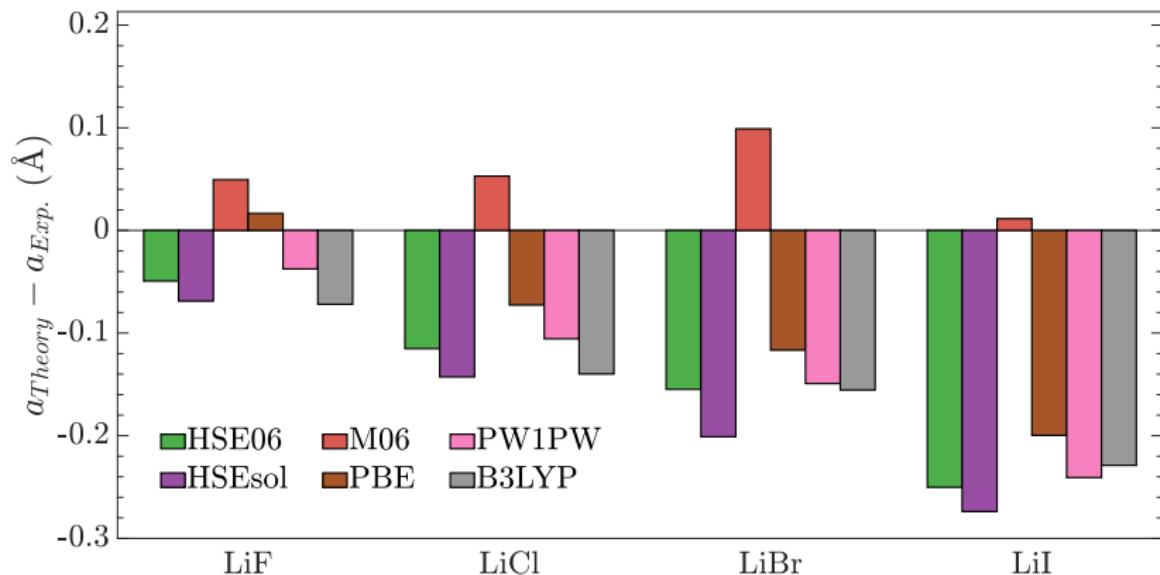
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How to choose the XC functional: comparison with experiment.

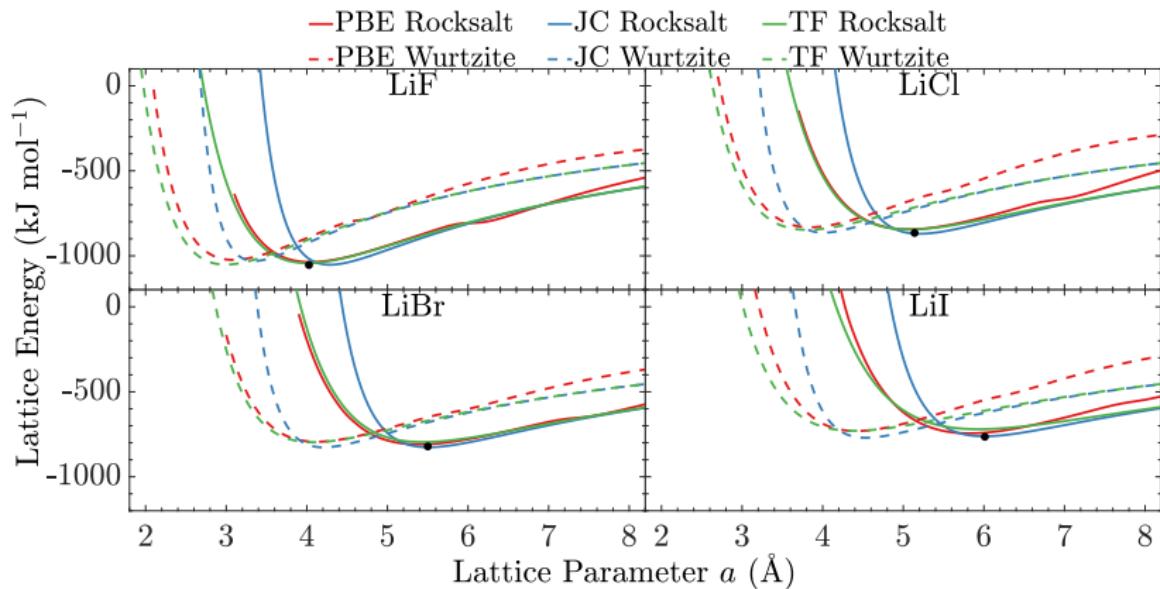


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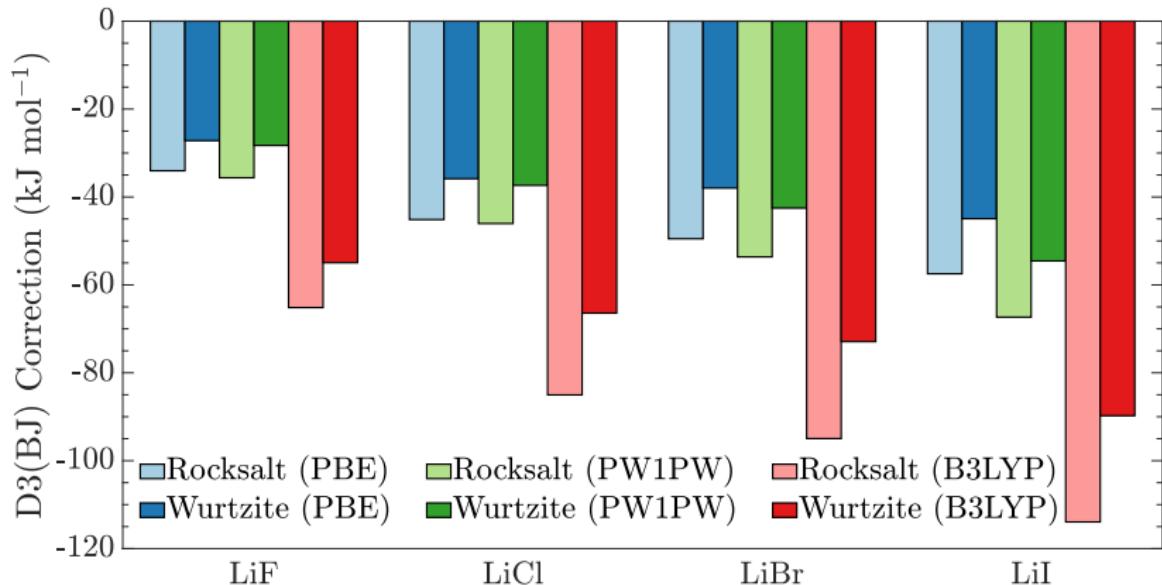
How to choose the XC functional: comparison with experiment.



Comparison of Potentials: Crystal Potential



Importance of Dispersion: Ab initio methods



Importance of Dispersion: Empirical models

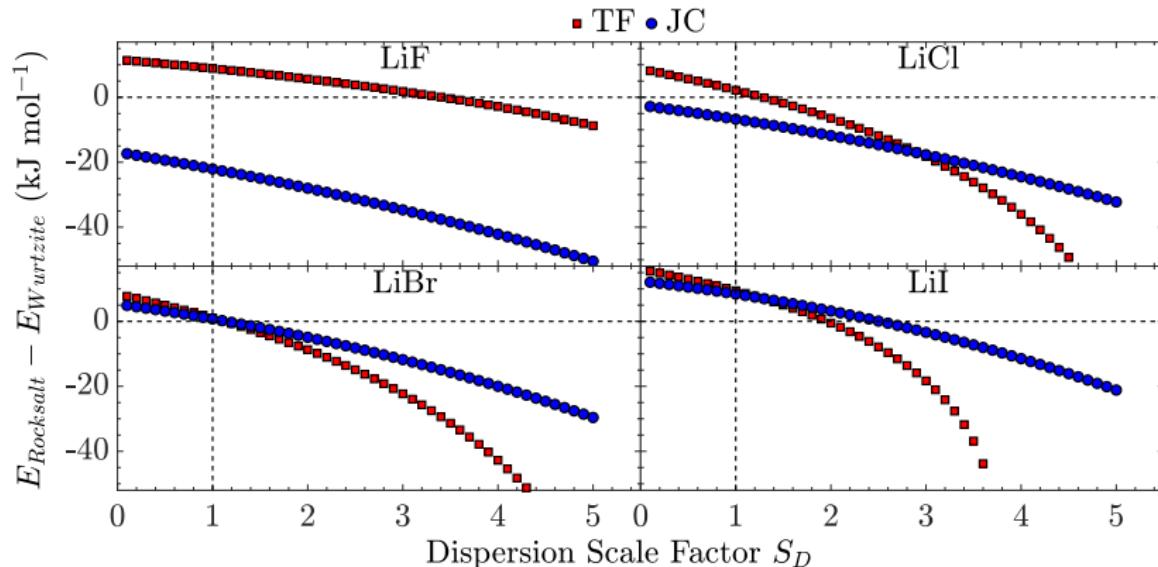
What if we **scale** the dispersion interaction in empirical models by a factor **S_D** ?

$$u_{ij}^{JC} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r} + 4\epsilon \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \mathbf{S_D} \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (5)$$

$$u_{ij}^{TF} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r} + B_{ij} e^{-\alpha_{ij} r} - \mathbf{S_D} \left(\frac{C_{ij}}{r^6} + \frac{D_{ij}}{r^8} \right) \quad (6)$$

Importance of Dispersion: Empirical models

What if we **scale** the dispersion interaction in empirical models by a factor S_D ?



Summary

In my research so far, we have found:

- TF empirical model favours wurtzite in all cases, yet its PES matches best with ab initio calculations.
- JC empirical model favours rocksalt in LiF and LiCl, but has incorrect energies at high pressure.
- Ab initio calculations show that wurtzite and rocksalt are very close in energy.
- The dispersion interaction is weak but favours rocksalt in both DFT calculations and empirical models.

Future Work: Nucleation Mechanism of LiX

With a working model for the lithium halides, can explore
non-classical nucleation mechanisms.

Unanswered Questions:

- Why does dispersion favour rocksalt?
- Is there a single free energy barrier to LiX nucleation?
- How does ion size affect the nucleation mechanism?
- Why does LiF solubility decrease at higher temperatures?

Acknowledgments

Thank you to the following for making this research possible:

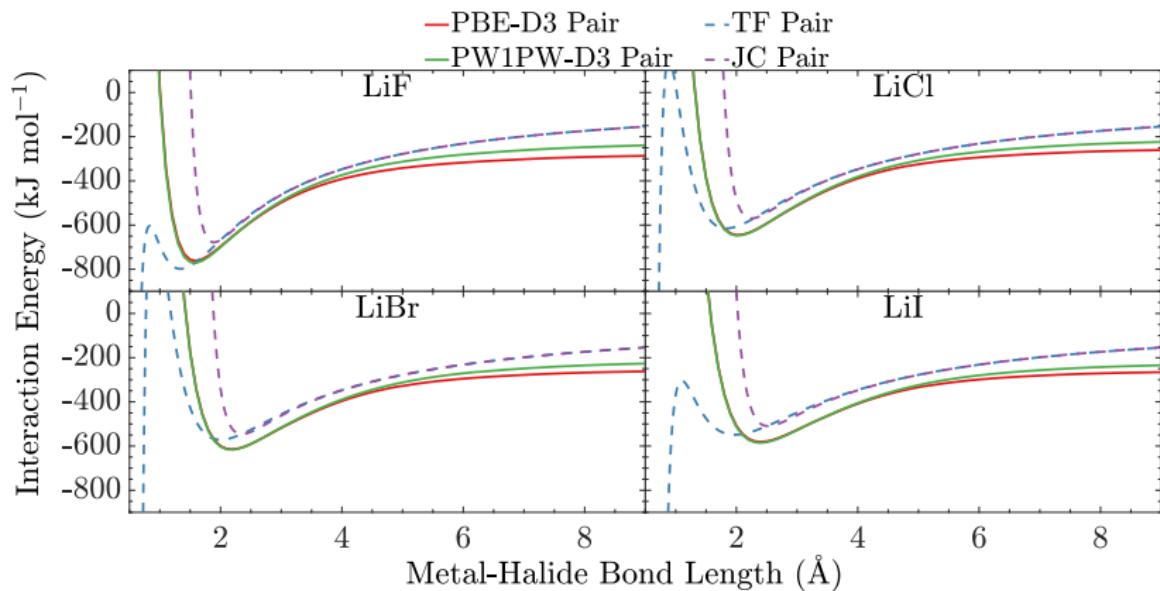
Prof. Gren Patey, Supervisor



THE UNIVERSITY OF BRITISH COLUMBIA

Chemistry
Faculty of Science

Comparison of Potentials: Pair Potential



JC With Different Water Models

Species	Model	Favoured	Rocksalt E_L	Wurtzite E_L	ΔE_L	a_{Rock}	a_{Wurtz}
LiF	Experimental	Rocksalt	-1054(1)			4.02620(5)	
	JC (SPC/E)	Rocksalt	-1052.59	-1030.51	-22.08	4.29	3.35
	JC (TIP3P)	Rocksalt	-1093.77	-1073.72	-20.05	4.09	3.19
	JC (TIP4P _{EW})	Rocksalt	-1059.52	-1041.3	-18.22	4.23	3.3
	TF	Wurtzite	-1043.11	-1051.97	8.86	4.01	2.99
LiCl	Experimental	Rocksalt	-865(2)			5.13988(4)	
	JC (SPC/E)	Rocksalt	-870.32	-863.58	-6.74	5.2	4.01
	JC (TIP3P)	Wurtzite	-891.53	-899.88	8.35	5.08	3.84
	JC (TIP4P _{EW})	Wurtzite	-877.65	-883.34	5.69	5.14	3.91
	TF	Wurtzite	-844.73	-846.9	2.17	5.08	3.81
LiBr	Experimental	Rocksalt	-821(2)			5.501(6)	
	JC (SPC/E)	Wurtzite	-826.03	-826.78	0.75	5.51	4.21
	JC (TIP3P)	Wurtzite	-836.91	-853.04	16.13	5.43	4.07
	JC (TIP4P _{EW})	Wurtzite	-826.72	-842.58	15.86	5.49	4.12
	TF	Wurtzite	-795.68	-796.72	1.04	5.44	4.08
LiI	Experimental	Rocksalt	-764(1)			6.012(7)	
	JC (SPC/E)	Wurtzite	-761.78	-770.2	8.42	6	4.54
	JC (TIP3P)	Wurtzite	-768.97	-790.37	21.4	5.91	4.4
	JC (TIP4P _{EW})	Wurtzite	-760.92	-782.98	22.06	5.98	4.45
	TF	Wurtzite	-720.06	-729.49	9.43	5.93	4.39

Born-Oppenheimer Approximation

$$\hat{\mathcal{H}}\Psi = E\Psi$$

where

$$\hat{\mathcal{H}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}.$$

Assume

$$\Psi(\vec{r}_1, \dots, \vec{r}_N, \vec{R}_1, \dots, \vec{R}_M) = \Psi_{elec}(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M) \Psi_{nucl}(\vec{R}_1, \dots, \vec{R}_M).$$

$$\begin{aligned} \hat{\mathcal{H}}\Psi_{elec}\Psi_{nucl} &= -\frac{1}{2} \sum_{i=1}^N \Psi_{nucl} \left(\nabla_i^2 \Psi_{elec} \right) - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 \left(\Psi_{elec} \Psi_{nucl} \right) + \left(\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \Psi_{elec} \Psi_{nucl} \\ &\quad + \left(\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \Psi_{elec} \Psi_{nucl} - \left(\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right) \Psi_{elec} \Psi_{nucl} \\ &= \underbrace{\left(\left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right) \Psi_{elec} \right)}_{\text{Electronic Hamiltonian}} \Psi_{nucl} + \left(\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \Psi_{elec} \Psi_{nucl} \\ &\quad - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \left(\underbrace{(\nabla_A^2 \Psi_{elec})}_{\text{Neglect}} \Psi_{nucl} + \underbrace{(\nabla_A^2 \Psi_{nucl})}_{\text{Keep}} \Psi_{elec} + 2 \underbrace{(\nabla_A \Psi_{elec})(\nabla_A \Psi_{nucl})}_{\text{Neglect}} \right) \end{aligned}$$

Born-Oppenheimer Approximation

Neglecting the indicated terms on the previous slide yields

$$\begin{aligned}\hat{\mathcal{H}}\Psi_{elec}\Psi_{nucl} &\approx \left(\underbrace{\left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i} \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right)}_{\varepsilon_{elec}} \Psi_{nucl} + \left(\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right) \Psi_{elec} \Psi_{nucl} \right. \\ &\quad \left. - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} (\nabla_A^2 \Psi_{nucl}) \Psi_{elec} = E \Psi_{elec} \Psi_{nucl} \right)\end{aligned}$$

The electronic problem is solved separately, with the nuclear degrees of freedom treated parametrically to yield ε_{elec} . The nuclear problem can then be solved separately as

$$\left(-\frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 + \underbrace{\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{\text{P.E. landscape for nuclear motion}} + \varepsilon_{elec} \right) \Psi_{nucl} = E \Psi_{nucl}$$

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If one wishes to do MD in this way, the electronic problem must be re-solved for each time step.

DFT: Kohn-Sham Method

The Kohn-Sham method for the ground electronic state. Start with the electronic problem

$$\hat{\mathcal{H}}_{elec} \Psi_i = E_i \Psi_i$$

where Ψ_i is the many-electron wavefunction. The Hamiltonian is

$$\hat{\mathcal{H}}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \underbrace{\left(\sum_{A=1}^M \frac{Z_A}{r_{iA}} \right)}_{V(\vec{r}_i)}.$$

In KS DFT this problem is converted into

$$\hat{\mathcal{H}}_{eff} \psi_i = \varepsilon_i \psi_i$$

where ψ_i are one-electron functions and

$$\hat{\mathcal{H}}_{eff} = -\frac{1}{2} \nabla^2 + V_{eff}.$$

V_{eff} is the mean-field effective potential created by the nuclei and other electrons acting on the electron of interest. It contains the external potential $V(\vec{r}_i)$, the electron-electron Coulomb potential, the exchange potential, and the correlation potential.

The premise of KS DFT: one can work with electron density $\rho(\vec{r})$ instead of the many-electron wavefunction $\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$. This is shown in the theorems of Kohn and Sham.

DFT: Kohn-Sham Method: Theorem 1

Theorem 1: the external potential, $V(\vec{r})$, acting on a fully-interacting system of N electrons in its ground state is determined (within an additive constant) by the electron density.

Proof: by contradiction.

Imagine you have two different external potentials, $V(\vec{r})$ and $V'(\vec{r})$, differing by more than a constant and leading to the same electron density $\rho(\vec{r})$ in the ground state.

$$\begin{aligned} V(\vec{r}) &\rightarrow \hat{\mathcal{H}} \\ V'(\vec{r}) &\rightarrow \hat{\mathcal{H}}'. \end{aligned}$$

These Hamiltonians have the same kinetic and electron-electron terms, but differ in their nuclear-electron term. Applying these two the electronic Schrödinger equation leads to

$$\begin{aligned} \hat{\mathcal{H}}\Psi_0 &= E_0\Psi_0 \\ \hat{\mathcal{H}}'\Psi'_0 &= E'_0\Psi'_0. \end{aligned}$$

The variational theorem tells us that $\langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle > E_0$ and $\langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle > E_0$. Writing this explicitly,

$$\begin{aligned} \langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle &= \int \Psi'^*_0(\vec{r}_1, \dots, \vec{r}_N) \left(\frac{-1}{2} \sum_{i=1}^N \nabla_i^2 \right) \Psi'_0(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N \\ &\quad + \int \Psi'^*_0(\vec{r}_1, \dots, \vec{r}_N) \left(\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right) \Psi'_0(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N \\ &\quad + \int \Psi'^*_0(\vec{r}_1, \dots, \vec{r}_N) \left(\sum_{i=1}^N V(\vec{r}_i) \right) \Psi'_0(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N. \end{aligned}$$

DFT: Kohn-Sham Method: Theorem 1

We can also write this as

$$\langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle = T' + E'_{ee} + \int \Psi'^*_0(\vec{r}_1, \dots, \vec{r}_N) \left(\sum_{i=1}^N \int V(\vec{r}) \delta(\vec{r} - \vec{r}_i) d\vec{r} \right) \Psi'_0(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N,$$

where the inner integral collapses due to the delta function $\delta(\vec{r} - \vec{r}_i)$. Rearranging,

$$\begin{aligned} \langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle &= T' + E'_{ee} + \underbrace{\int V(\vec{r}) d\vec{r} \int \Psi'^*_0(\vec{r}_1, \dots, \vec{r}_N) \left(\sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \right) \Psi'_0(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N}_{\text{Electron Density}} \\ &= T' + E'_{ee} + \int V(\vec{r}) \rho(\vec{r}) d\vec{r} > E_0 \quad (\text{assumption}). \end{aligned}$$

Now we also have

$$\langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle = \dots = T + E_{ee} + \int V'(\vec{r}) \rho(\vec{r}) d\vec{r} > E'_0.$$

We can also write

$$E_0 < \langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{\mathcal{H}} - \hat{\mathcal{H}}' | \Psi'_0 \rangle \langle \Psi'_0 | \hat{\mathcal{H}}' | \Psi'_0 \rangle = \int (V(\vec{r}) - V'(\vec{r})) \rho(\vec{r}) d\vec{r} + E'_0.$$

DFT: Kohn-Sham Method: Theorem 1

So far we have

$$E_0 < E'_0 + \int (V(\vec{r}) - V'(\vec{r})) \rho(\vec{r}) d\vec{r}, \quad (5)$$

but we can also write

$$\begin{aligned} E'_0 &< \langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle = \int (V'(\vec{r}) - V(\vec{r})) \rho(\vec{r}) d\vec{r} + E_0 \\ E'_0 &< E_0 - \int (V(\vec{r}) - V'(\vec{r})) \rho(\vec{r}) d\vec{r} \end{aligned} \quad (6)$$

Now add equations 5 and 6 to get

$$E_0 + E'_0 < E_0 + E'_0$$

which is a contradiction. Hence our original assumption that two different external potentials can lead to the same electron density is wrong. This means that $\rho(\vec{r})$ uniquely determines $V(\vec{r})$ which uniquely determines the one electron Hamiltonian $\hat{\mathcal{H}}$ which uniquely determines the ground state energy and wavefunction. The problem of $3N$ variables can be rewritten as a problem of 3 variables.

DFT: Kohn-Sham Method: Theorem 2

Theorem 2: The variation principle in terms of electron density.

Proof: Assume $\rho(\vec{r})$ is the correct ground state density and $\rho'(\vec{r})$ is a trial density. From theorem 1, we saw that the ground state energy can be written as a functional of the electron density

$$E_0[\rho(\vec{r})] = \underbrace{T[\rho(\vec{r})] + U_{ee}[\rho(\vec{r})]}_{F_{HK}[\rho(\vec{r})]} + \int V(\vec{r})\rho(\vec{r})d\vec{r}.$$

The arbitrary trial density $\rho'(\vec{r})$ uniquely defines a wavefunction Ψ'_0 , but we know from the variational principle that

$$\langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle \geq E_0.$$

But theorem 1 showed us that

$$\langle \Psi'_0 | \hat{\mathcal{H}} | \Psi'_0 \rangle = F_{HK}[\rho(\vec{r})] + \int V(\vec{r})\rho(\vec{r})' d\vec{r}.$$

Hence

$$F_{HK}[\rho(\vec{r})] + \int V(\vec{r})\rho(\vec{r})' d\vec{r} \geq E_0.$$

From theorem 1, the equality is true only if $\rho'(\vec{r}) = \rho(\vec{r})$.

DFT: Kohn-Sham Method

From theorems 1 and 2, we know that the external potential is fully determined if the electron density is known. That means we can work with $\rho(\vec{r})$ instead of the all electron wavefunction, i.e. 3 variables instead of $3N$. The Kohn-Sham method is to imagine a reference system of non-interacting electrons,

$$\hat{\mathcal{H}}_{\text{ref}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{\text{ref}}(\vec{r}_i),$$

which would lead to the one-electron problem

$$\hat{\mathcal{H}}_{\text{ref}} \psi_i = \varepsilon_i \psi_i.$$

The key is to choose $V_{\text{ref}}(\vec{r}_i)$ (the external potential of the reference system) such that the electron density of this reference system is equal to the electron density of the actual system of interest. This (after a fairly long derivation) leads to the Kohn-Sham equations

$$\hat{\mathcal{H}}_{\text{eff}} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r})$$

where

$$V_{\text{eff}}(\vec{r}) = V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{XC}[\rho(\vec{r})]}{\delta \rho(\vec{r})}$$
$$\rho(\vec{r}) = \sum_{i=1}^N \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

The one-electron orbitals are given by

$$\hat{\mathcal{H}}_{\text{eff}} \psi_i = \varepsilon_i \psi_i.$$

DFT: Kohn-Sham Method Summary

The Kohn-Sham Method:

Begin with N trial wavefunctions $\{\psi_i\}$

$$1) \quad \rho(\vec{r}) = \sum_{i=1}^N \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

$$2) \quad V_{\text{eff}} = V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \underbrace{\frac{\delta E_{XC}[\rho(\vec{r})]}{\delta \rho(\vec{r})}}_{V_{XC}[\rho(\vec{r})]}$$

$$3) \quad \hat{\mathcal{H}}_{\text{eff}} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r})$$

$$4) \quad \hat{\mathcal{H}}_{\text{eff}} \psi_i = \varepsilon_i \psi_i$$

Repeat steps 1-4 until energy is sufficiently converged between cycles. Once convergence is achieved, the total energy is calculated as a functional of the electron density:

$$E[\rho(\vec{r})] = \sum_{i=1}^N \int \psi_i^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\vec{r}) d\vec{r} + \int V(\vec{r}) \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + E_{XC}[\rho(\vec{r})]$$

or equivalently

$$E[\rho(\vec{r})] = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int \frac{\rho(\vec{r}') \rho(\vec{r})}{|\vec{r}' - \vec{r}|} d\vec{r}' d\vec{r} + E_{XC}[\rho(\vec{r})] - \int \frac{\delta E_{XC}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \rho(\vec{r}) d\vec{r}'$$

Ewald Summation

The total interaction energy of a 3D periodic system of point charges is

$$E = \frac{1}{4\pi\epsilon_0} \sum_{\mathbf{n}} \frac{1}{2} \sum_{i=1}^N \sum'_{j=1}^N \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}|}$$

where $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ are periodic, but this straightforward sum is only conditionally convergent, and converges slowly.

Ewald summation converts this conditionally convergent sum in real space into two quickly and absolutely convergent sums: one in real space and one in reciprocal (\mathbf{k}) space.

Ewald Summation

Ewald summation relies on the fact that the charge distribution is **periodic**. It takes a **Fourier transform** of the long range interaction.

$$\begin{aligned} E &= E^S + E^L - E^{\text{self}} \\ &= \frac{1}{4\pi\varepsilon_0} \frac{1}{2} \sum_{\mathbf{n}} \sum_{i=1}^N \sum'_{j=1}^N \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{nL}|} \operatorname{erfc}\left(\frac{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{nL}|}{\sqrt{2}\sigma}\right) \\ &\quad + \frac{1}{2V\varepsilon_0} \sum_{\mathbf{k} \neq 0} \frac{e^{-\sigma^2 k^2/2}}{k^2} |S(\mathbf{k})|^2 - \frac{1}{4\pi\varepsilon_0} \frac{1}{\sqrt{2\pi}\sigma} \sum_{i=1}^N q_i^2 \end{aligned}$$

Self correction term corrects the long range summation, which includes the self interaction in order to maintain the **periodicity of the interaction**.

Ewald Summation

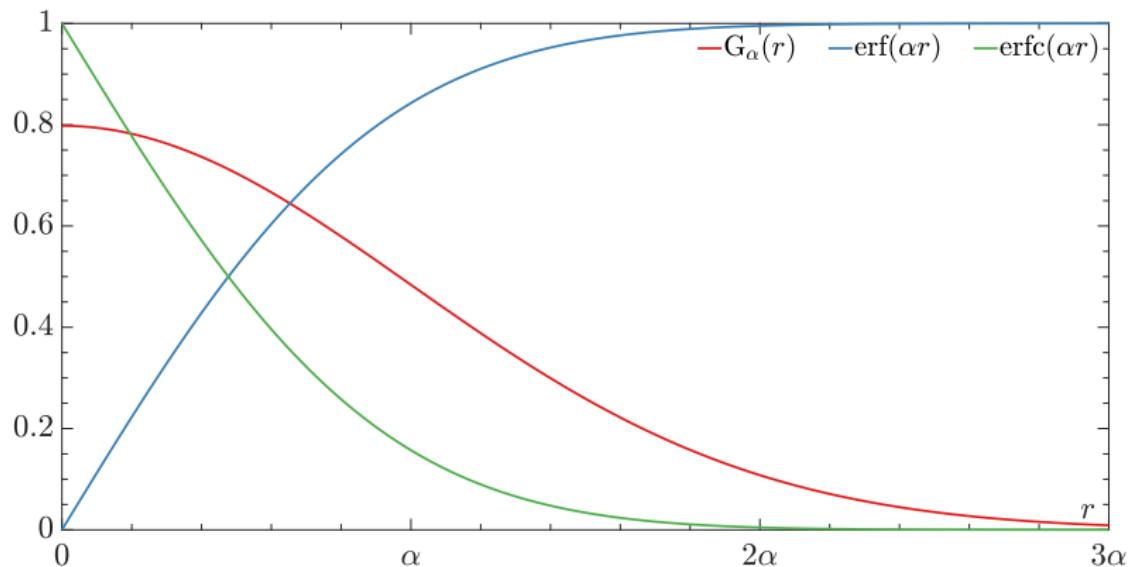
$$S(\mathbf{k}) \equiv \sum_{i=1}^N q_i e^{i\mathbf{k} \cdot \mathbf{r}_i}$$

is the structure factor of charge distribution. The way that the Ewald sum has been written in the previous slide assumes that the infinite periodic crystal is surrounded by a perfectly conducting boundary, which neutralizes the net dipole moment. With an infinite dielectric constant, or when the unit cell has no dipole moment, this term is zero.

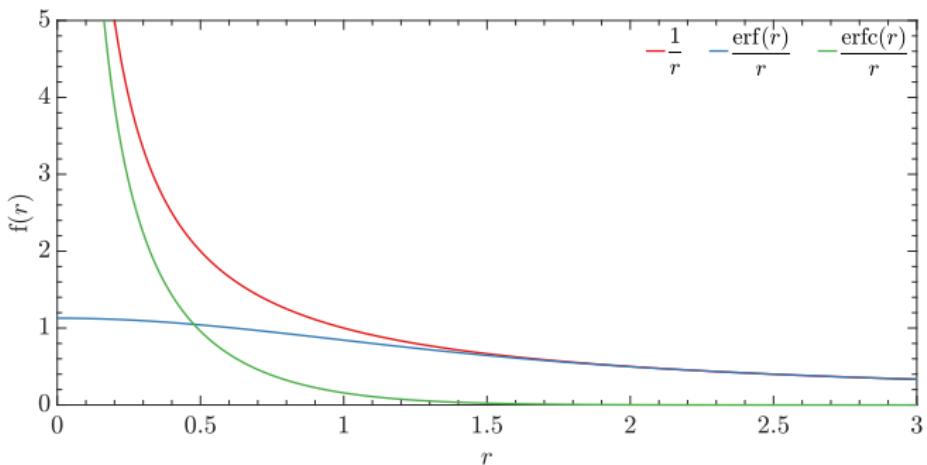
If one wishes to use vacuum boundaries (dielectric constant = 1), then an additional surface dipole term is needed

$$E_{\text{Dipole}} = \frac{1}{6\epsilon_0 V} \left| \sum_{i=1}^N q_i \mathbf{x}_i \right|^2$$

Ewald Summation



Ewald Summation



The basic idea is to separate the fast variation part for small r and the smooth part for large r . In particular, the first part should decay fast and be negligible beyond some cutoff distance, whereas the second part should be smooth for all r , such that its Fourier transform can be represented by a few terms.

Born–Landé Equation from 1918

An early attempt at constructing an equation for the lattice energy came from the Born–Landé model, which hypothesized that the crystal energy was

$$E(r) = \frac{MZ^+Z^-e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

Differentiating with respect to r and solving for the unknown B yields

$$E_{Lattice} = \frac{MZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right).$$

Born-Mayer Equation from 1932

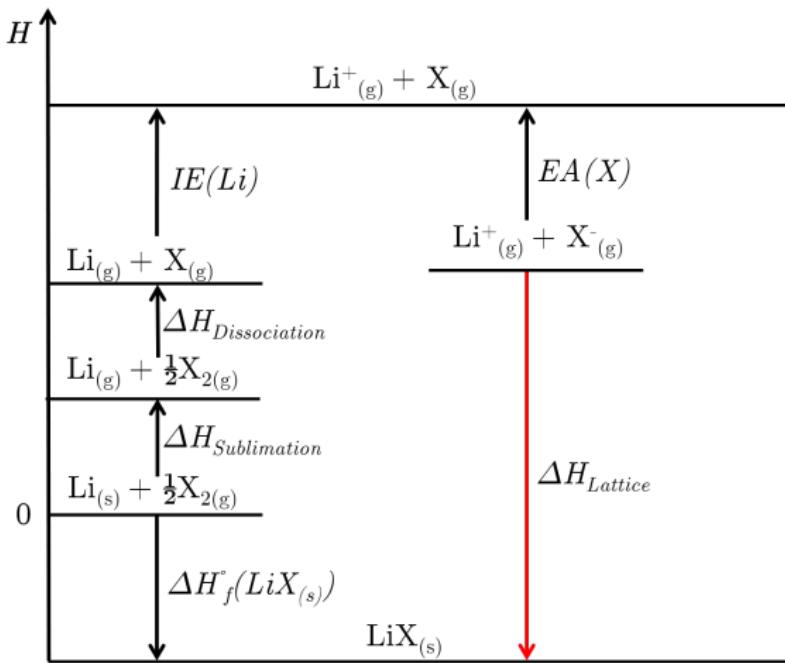
A slightly better attempt at an equation for the lattice energy came from the Born-Mayer model,

$$E(r) = \frac{MZ^+Z^-e^2}{4\pi\epsilon_0 r} + B \exp\left(\frac{-r}{\rho}\right).$$

Differentiating with respect to r and solving for the unknown B yields

$$E_{Lattice} = \frac{MZ^+Z^-e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right).$$

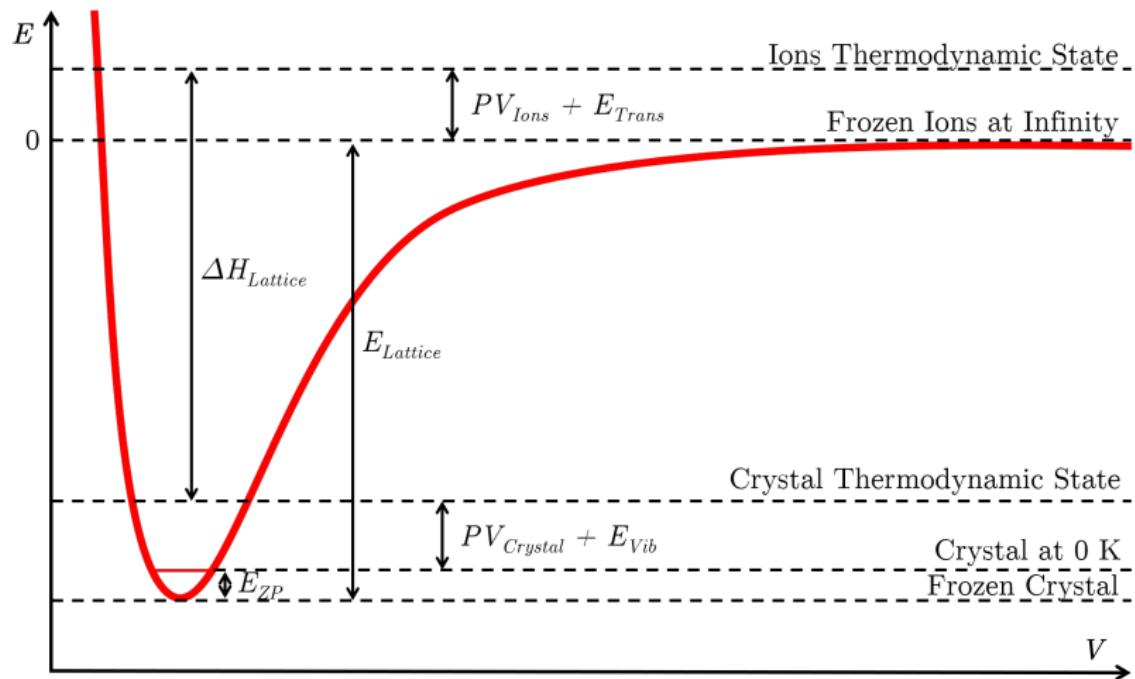
Born-Haber Cycle for Lattice Energies



Experimental Lattice Enthalpies

$$\begin{aligned}\Delta H_{Lattice} = & \Delta H_f^\circ(\text{LiX}_{(s)}) \\ & + \Delta H_{Sub}(Li) \\ & + \Delta H_{Dissociation}(X_2) \\ & + IE(Li) \\ & - EA(X)\end{aligned}$$

Lattice Enthalpy vs Energy



Lattice Energy from Enthalpy

$$\begin{aligned}\Delta H_{Lattice} &= H_{Crystal} - H_{Ions} \\ &= E_{Crystal} + (PV)_{Crystal} - E_{Ions} - (PV)_{Ions}.\end{aligned}$$

Assume $P_{Crystal} = P_{Ions} = P = 1\text{ bar}$ and constant $T = 298.15$.

$$\begin{aligned}\Delta H_{Lattice} &= V_{Crystal} + E_{ZP} + E_{Vib} + PV_{Crystal} - V_{Ions} - E_{Trans} - PV_{Ions} \\ &= E_{Lattice} + E_{ZP} + E_{Vib} - E_{Trans} + P\Delta V.\end{aligned}$$

Assume the molar volume of the crystal is 0, and assume ions are ideal so $PV = nRT$.

$$\Delta H_{Lattice} = E_{Lattice} + E_{ZP} + E_{Vib} - E_{Trans} + \Delta nRT$$

where $\Delta n = (-n_{ions})$.

Lattice Energy from Enthalpy

So ignoring volume of crystal, assuming ideal gas behaviour, and assuming constant T and P we have for a salt M_aX_b

$$E_{Lattice} = \Delta H_{Lattice} - E_{ZP} - E_{Vib} + E_{Trans} + (a + b)RT.$$

In practice the zero point vib. energy is ignored, and the vibrational energy is assumed $E_{Vib} = 3nRT$ (high T classical limit). Likewise, the ions translational energy is assumed $E_{Trans} = \frac{3}{2}nRT$ yielding

$$E_{Lattice} = \Delta H_{Lattice} - 3(a + b)RT + \frac{3}{2}(a + b)RT + (a + b)RT$$

$$E_{Lattice} = \Delta H_{Lattice} - \left[a\left(\frac{3}{2} - 2\right) + b\left(\frac{3}{2} - 2\right) \right] RT.$$

Gaussian Basis Sets

In general, molecular orbitals are created by linear combination of atomic orbitals

$$\Psi_i(\mathbf{r}) = \sum_{\mu=1}^K c_{\mu i} \Phi_{\mu}(\mathbf{r}).$$

When using a Gaussian basis set, each atomic orbital is itself a linear combination (a “contraction”) of 3D primitive Gaussian functions multiplied by a spherical harmonic $Y_{\ell m}(\theta, \phi)$, which are centered in space on an atomic nucleus A .

$$\Phi_A(\mathbf{r}) = R_{A\ell}(\mathbf{r}) Y_{\ell m}(\theta, \phi)$$

$$R_{A\ell}(\mathbf{r}) = (\mathbf{r} - \mathbf{r}_A)^{\ell} \sum_j c_j B(\ell, \alpha_j) \exp(-\alpha_j (\mathbf{r} - \mathbf{r}_A)^2).$$

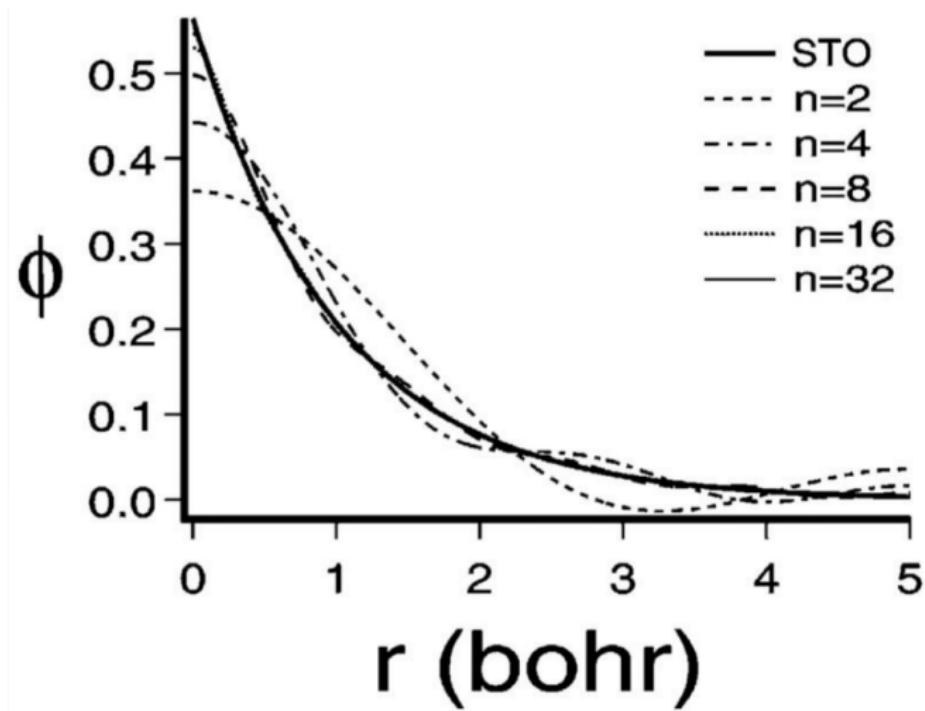
where $B(\ell, \alpha_j)$ is a normalization constant which insures that
 $\int d\mathbf{r} |B(\ell, \alpha_j) \exp(-\alpha_j (\mathbf{r} - \mathbf{r}_A)^2)|^2 = 1.$

Gaussian Basis Sets: Minimal

- A minimal basis set is constructed using only one atomic orbital function of each type occupied in the atom(s) of the basis set.
- For example, Lithium has $1s^2 2s^1$ so a minimal basis set uses two contracted sets of *s*-type Gaussians, one for the $1s$ electrons and one for the $2s$ electron.
- The most common minimal basis set is STO- nG , where n is an integer.
- These “Slater-Type Orbitals” are each made from a linear combination (contraction) of n primitive Gaussians. Only the minimum number of atomic orbitals are used.
- Slater orbitals are similar to primitive Gaussians, but have a more physical shape with a **cusp**.

$$R_{An}(\mathbf{r}) = (\mathbf{r} - \mathbf{r}_A)^{n-1} N \exp(-\xi(\mathbf{r} - \mathbf{r}_A)).$$

Gaussian Basis Sets: Slater Orbitals



Gaussian Basis Sets: Notation

- Core electrons are tightly bound, and are not affected much by nearby atoms.
- Split valence: only one basis function for core AOs, and more basis functions for valence AOs
- pob-TZVP basis set has so-called “triple-zeta valence” quality. This means it has three times as many atomic orbitals as a minimal basis set would for the same atom for the valence orbitals. The core electrons are treated minimally.
- The “P” in pob-TZVP indicates that there is an additional set of polarization functions. To polarize a basis function with angular momentum ℓ , one mixes it with basis functions of angular momentum $\ell + 1$.
- Li: one atomic orbital for the $1s$ orbital, three atomic orbitals to describe the valence $2s$ orbital, plus one set of p -type Gaussian orbitals for polarization.

Gaussian Basis Sets: Pople Notation

- Pople notation is commonly used to describe Gaussian basis sets: usually looks like **X-YG**.
- **X** is an integer that indicates the number of contracted Gaussians used to describe each of the core electrons. Core orbitals are usually described by only one contracted Gaussian each.
- **Y** is a set of integers such as 311. The number of integers corresponds to the number of contracted Gaussians used to describe the valence orbitals. Each integer in this number is the number of contracted Gaussians in the atomic orbital.
- Example: 7-311G has 7 primitive Gaussians contracted into a single function for each core atomic orbital. The valence orbitals each have three functions, the first of which is made of three primitive Gaussians whereas each of the others is made from one primitive Gaussian.

Gaussian Basis Sets: Extra Notation

- Correlation consistent basis sets are augmented with successively larger shells of polarization. They are required for good quality post-HF calculations.
- 'cc-p', stands for 'correlation consistent polarized'.
- The prefix 'aug' means that the basis is augmented with diffuse functions, which more accurately represent the "tail" portion of the atomic orbitals.
- In pople notation * means extra polarization functions on non-H atoms, while ** includes H atoms.
- Similarly, + and ++ correspond to extra diffuse functions.

Exchange-Correlation Functionals: Local Density Approximation

Local spin density approximation (LSDA) XC functionals have the following general form

$$E_{LDSA}[\rho_{\downarrow}(\mathbf{r}), \rho_{\uparrow}(\mathbf{r})] = \int \rho(\mathbf{r}) \varepsilon_{XC}^{LDSA}[\rho_{\downarrow}(\mathbf{r}), \rho_{\uparrow}(\mathbf{r})] d\mathbf{r}.$$

XC energy density at each point in space assumed same as a homogeneous electron gas (HEG) with that electron density.

$$\varepsilon_{XC}^{LDSA}[\rho_{\downarrow}(\mathbf{r}), \rho_{\uparrow}(\mathbf{r})] = \frac{1}{2} \int \rho(\mathbf{r}') (\bar{g}^{HEG}[|\mathbf{r} - \mathbf{r}'|, \rho_{\downarrow}(\mathbf{r}), \rho_{\uparrow}(\mathbf{r})] - 1) d\mathbf{r}'$$

where \bar{g}^{HEG} is the averaged pair-correlation function in the homogeneous electron gas. $\rho(\mathbf{r}) = \rho_{\downarrow}(\mathbf{r}) + \rho_{\uparrow}(\mathbf{r})$.

Exchange-Correlation Functionals: Generalized Gradient Approximation

Improves on LSDA in the spirit of a Taylor expansion: depends on $\rho(r)$ but also $\nabla\rho(r)$

$$E_{GGA} [\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})] = \int f (\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}), \nabla\rho_{\uparrow}(\mathbf{r}), \nabla\rho_{\downarrow}(\mathbf{r})) d\mathbf{r}$$

where the function f depends on the particular GGA XC functional. f is usually designed such that

$$f (\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}), 0, 0) = \rho(\mathbf{r}) \varepsilon_{XC}^{LDSA} [\rho_{\downarrow}(\mathbf{r}), \rho_{\uparrow}(\mathbf{r})]$$

Exchange-Correlation Functionals: PBE

- Generalized Gradient Approximation class of XC functional.
- Designed to be entirely free of empirical parameters, while satisfying many energetically-significant conditions.

Method: Ab Initio Calculations

Comparison of Ab Initio methods:

HF Theory:

- Exact Coulomb.
- Exact Exchange.
- No Correlation.
- Mean-field.
- Scales N^4 .

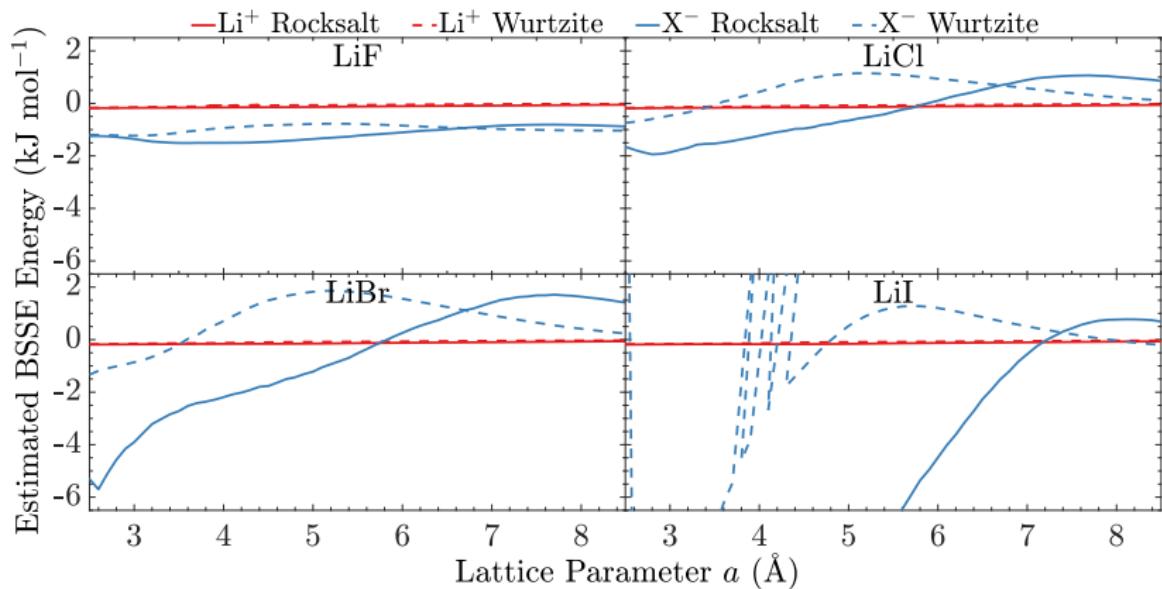
DFT:

- Exact Coulomb.
- Approx. Exchange.
- Approx. Correlation.
- Scales N^3 or N^4 .
- Based on electron density.
- Born-Oppenheimer approximation, neglect relativistic effects, incomplete basis Sets, and numerical approximations.

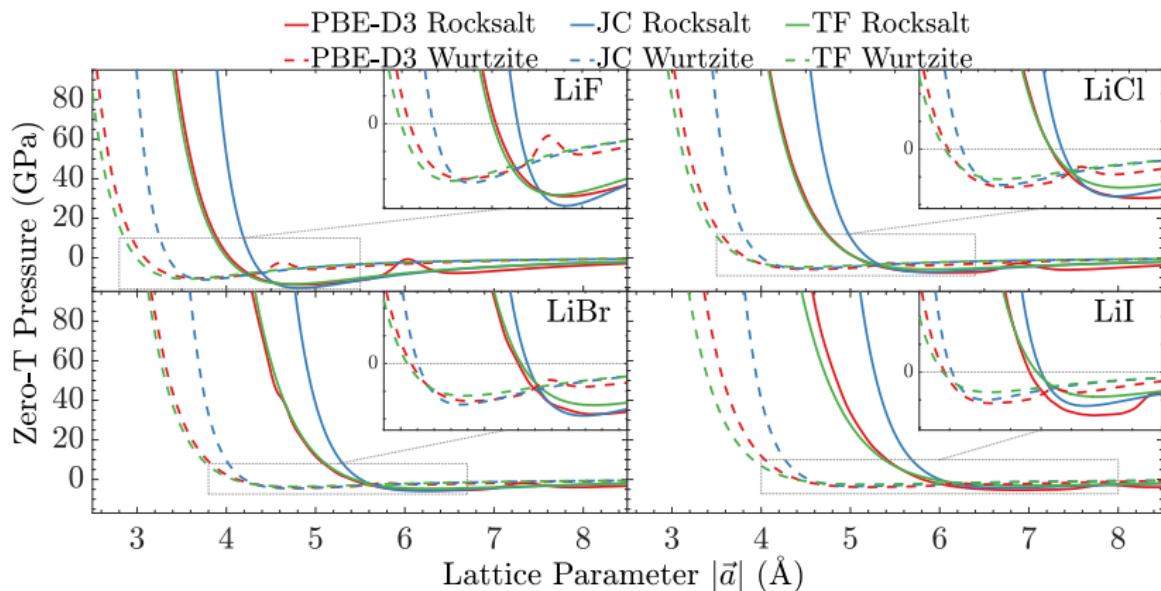
Post-HF Methods:

- Exact Coulomb.
- Exact Exchange.
- Accurate Approx. Correlation.
- Poor Scaling, often huge calculations.

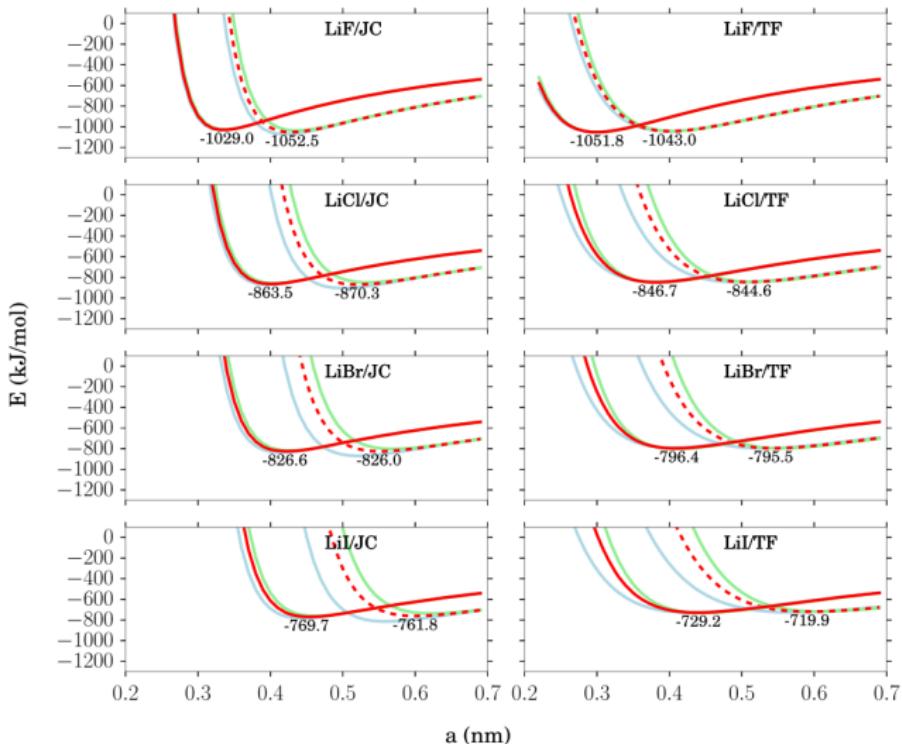
BSSE



Zero T Pressure vs a



Comparison of LiX Rocksalt vs Wurtzite for TF and JC



Importance of Dispersion

DFT does not take into account dispersion at large r : asymptotic interaction energy of local density functionals falls off exponentially.

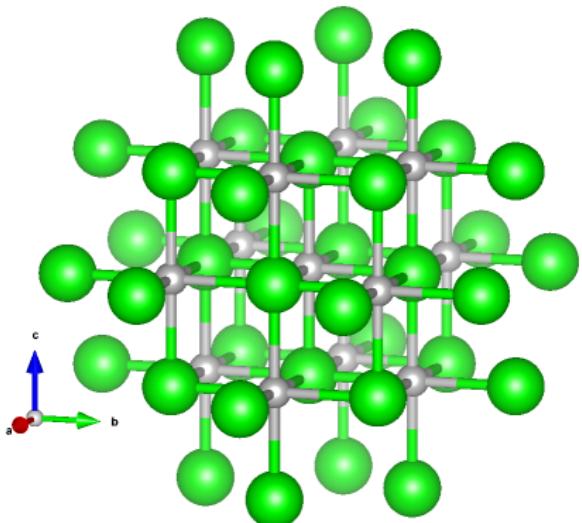
One solution:

Third generation dispersion (D3) with Becke-Johnson damping function:

$$E_{\text{disp}} = - \sum_{i>j} \left(\frac{C_{6,ij}}{R_{\text{vdW},ij}^6 + R_{ij}^6} + \frac{C_{8,ij}}{R_{\text{vdW},ij}^8 + R_{ij}^8} + \frac{C_{10,ij}}{R_{\text{vdW},ij}^{10} + R_{ij}^{10}} \right)$$

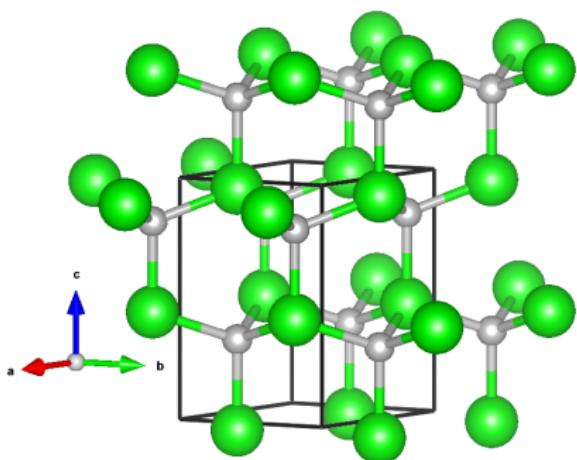
- $C_{n,ij}$ are parameter free, calculated on the fly from occupied orbitals and polarizabilities. Therefore, $C_{n,ij}$ change with the electronic environment.
- $R_{\text{vdW},ij}$ = sum of effective VdW radii of atoms i and j .

Rocksalt



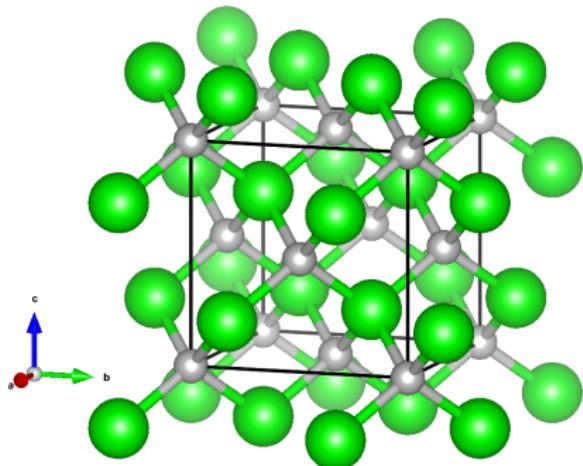
- Face centered cubic
- Space Group: $Fm\bar{3}m$ (225)
- $a = b = c$
- $\alpha = \beta = \gamma = 90^\circ$
- 8 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 6
- Nearest Neighbour bond length: $\frac{1}{2}a$
- Fractional Coordinates:
 $Li = (0, 0, 0)$ and
 $X = (\frac{1}{2}, 0, 0)$

Wurtzite



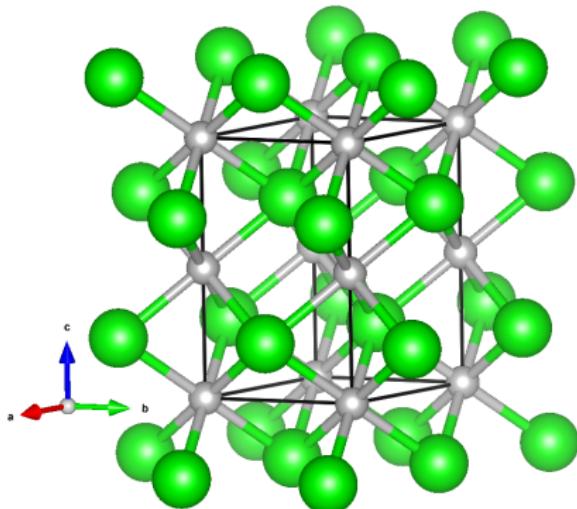
- Primitive Hexagonal
- Space Group: P6₃mc (186)
- $a = b = \sqrt{\frac{3}{8}}c$
- $\alpha = \beta = 90^\circ; \gamma = 120^\circ$
- 4 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 4
- Nearest Neighbour bond length: $\sqrt{\frac{3}{8}}a$
- Fractional Coordinates:
 $Li = (\frac{1}{3}, \frac{2}{3}, \frac{3}{8})$ and
 $X = (\frac{1}{3}, \frac{2}{3}, 0)$

Sphalerite (Zincblende)



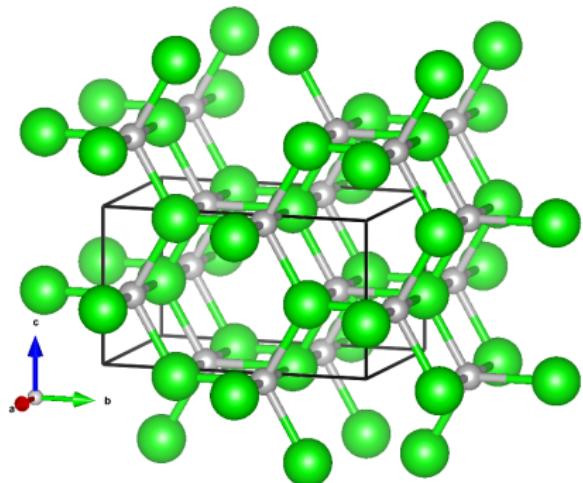
- Face Centered Cubic
- Space Group: $F\bar{4}3m$ (216)
- $a = b = c$
- $\alpha = \beta = \gamma = 90^\circ$
- 8 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 4
- Nearest Neighbour bond length: $\frac{\sqrt{3}}{4}a$
- Fractional Coordinates:
 $Li = (0, 0, 0)$ and
 $X = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$

NiAs (B8₁)



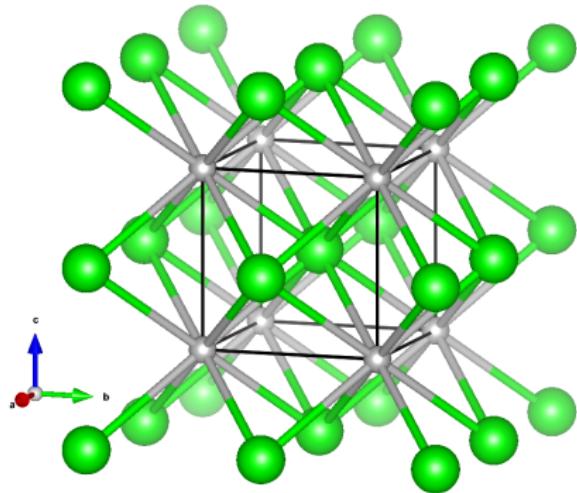
- Primitive Hexagonal
- Space Group: P_m⁶³mc (194)
- $a = b; c \approx 1.39a$ (variable)
- $\alpha = \beta = 90^\circ; \gamma = 120^\circ$
- 4 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 6
- Nearest Neighbour bond length: $\sqrt{\frac{a^2}{3} + \frac{c^2}{16}}$
- Fractional Coordinates:
Li = (0, 0, 0) and
 $X = (\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$

5-5



- Primitive Orthorhombic
- Space Group: Pnnm (58)
- $a = \frac{2}{3}b = \frac{2}{\sqrt{3}}c$
- $\alpha = \beta = \gamma = 90^\circ$
- 8 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 5
- Nearest Neighbour bond length: $\frac{1}{2}a$
- Fractional Coordinates:
 $\text{Li} = (\frac{1}{4}, \frac{1}{6}, \frac{1}{2})$ and
 $\text{X} = (\frac{1}{4}, \frac{1}{3}, 0)$

CsCl



- Primitive Cubic
- Space Group: $Pm\bar{3}m$ (221)
- $a = b = c$
- $\alpha = \beta = \gamma = 90^\circ$
- 2 Atoms in Unit Cell
- 2 Atoms in Asym. Unit
- Coordination number: 8
- Nearest Neighbour bond length: $\frac{\sqrt{3}}{2}a$
- Fractional Coordinates:
 $Li = (0, 0, 0)$ and
 $X = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

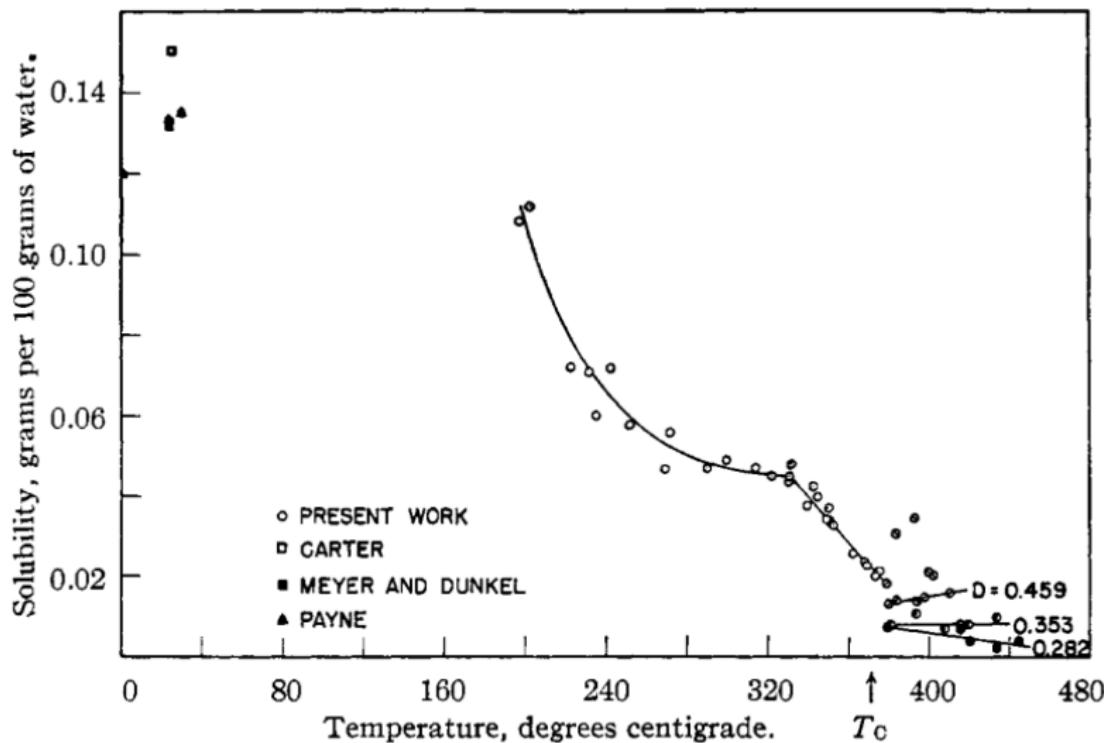


Fig. 11.—Solubility of lithium fluoride in water.

Radius Ratio Rules

From traditional ionic radii:

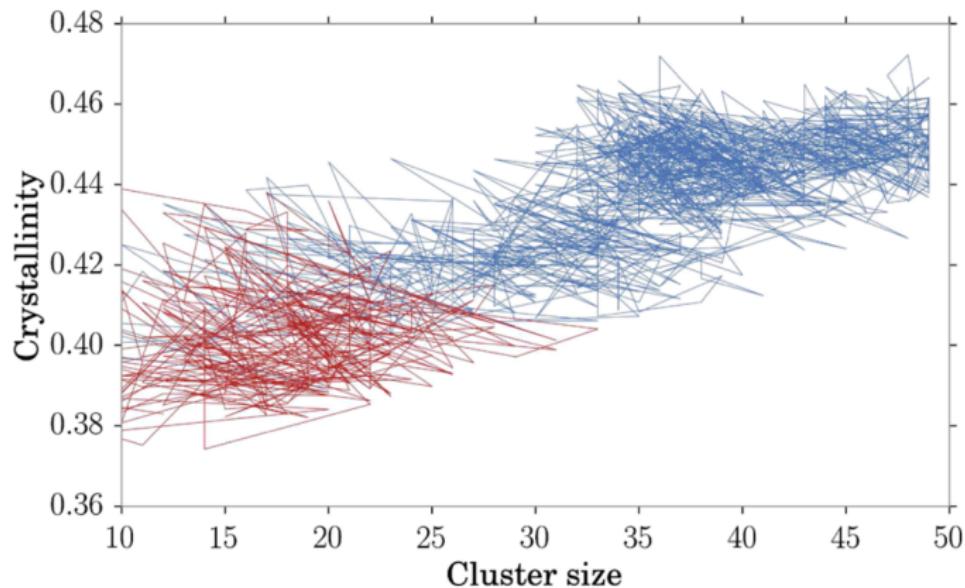
Salt	Radius Ratio	Predicted Structure
LiF	0.7563	Primitive Cubic (CsCl)
LiCl	0.5389	Rocksalt
LiBr	0.4945	Rocksalt
LiI	0.4369	Rocksalt
NaCl	0.6949	Rocksalt

Radius Ratio Rules

Using JC σ parameter as the “radius”:

Salt	Radius Ratio	Predicted Structure	Observed Structure
LiF	0.3505	Wurtzite	Rocksalt
LiCl	0.2918	Wurtzite	Rocksalt
LiBr	0.2875	Wurtzite	Wurtzite
LiI	0.2710	Wurtzite	Wurtzite
NaCl	0.4471	Rocksalt	Rocksalt

NaCl Nucleation vs Size and Crystallinity



Failed nucleation clusters are shown in red, while successful nucleation clusters are shown in blue.

NaCl Nucleation vs Size and Crystallinity

The dependence on size is in agreement with CNT, but crystallinity is defined as the average of q_8 over an entire cluster. For a particular ion,

$$q_I = \left[\frac{4\pi}{2I+1} \sum_{m=-I}^I |q_{Im}|^2 \right]^{1/2}$$

and

$$q_{Im} = \frac{1}{N} \sum_{r_i=r_1}^{r_N} Y_I^m(\theta(\mathbf{r}_i), \phi(\mathbf{r}_i)).$$

The number 8 was chosen empirically for best separation between liquid and solid phase ions. Here $N = 12$ is the number of nearest neighbor ions.

Lorenz-Berthelot combining rules

In the JC model, Lennard-Jones parameters are only defined between ions/atoms of the same type. To find the parameters for mixed interactions, the Lorenz-Berthelot combining rules are used:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$
$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

So the radius of the Lennard-Jones well is the arithmetic mean of the two radii, and the well depth is the geometric mean.

The Gibbs Relations

The first law of thermodynamics states $dU = dq + dw$. For a reversible process, $dq = \frac{dS}{T}$ and $dw = -PdV$, hence

$$dU = TdS - PdV$$

for tiny changes in the internal energy “at equilibrium.” From this, increments of $H \equiv U + PV$; $A \equiv U - TS$; and $G \equiv H - TS$ can be similarly defined:

$$dH = TdS + VdP,$$

$$dA = -SdT - PdV,$$

$$dG = -SdT + VdP.$$

The Gibbs Relations

From the form of the thermodynamic potentials in differential form:

$$dU = TdS - PdV,$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV,$$

$$dG = -SdT + VdP.$$

We can derive the following mathematical equivalencies

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \left(\frac{\partial U}{\partial V} \right)_S = -P \quad \left(\frac{\partial H}{\partial S} \right)_P = T \quad \left(\frac{\partial H}{\partial P} \right)_S = V$$
$$\left(\frac{\partial A}{\partial T} \right)_V = -S \quad \left(\frac{\partial A}{\partial V} \right)_T = -P \quad \left(\frac{\partial G}{\partial T} \right)_P = -S \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

The Maxwell Relations

From the thermodynamic potentials in differential form:

$$\begin{aligned} dU &= TdS - PdV, & dH &= TdS + VdP \\ dA &= -SdT - PdV, & dG &= -SdT + VdP. \end{aligned}$$

and the equivalency of mixed partial derivatives, we can obtain the Maxwell relations:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, & \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P, \\ -\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V, & \left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P. \end{aligned}$$

Heat Capacities

The definition of heat capacity is

$$C \equiv \frac{dq}{dT}$$

At constant volume (assuming only PV work is allowed) we have $dw = -P_{ext}dV = 0$. Therefore, the first law tells us $dU_V = dq_V$ and constant volume heat capacity is just

$$C_V = \frac{dU_V}{dT_V} = \left(\frac{\partial U}{\partial T} \right)_V.$$

Similarly at constant pressure,

$$C_P = \frac{dH_P}{dT_P} = \left(\frac{\partial H}{\partial T} \right)_P.$$

Time-Independent Schrodinger Equation

The de Broglie wavelength equation is

$$\lambda = \frac{h}{p}$$

and the total energy of a particle is just

$$E = \frac{p^2}{2m} + V(x) \rightarrow p = \sqrt{2m(E - V(x))}.$$

Plugging this into the de Broglie wave equation yields

$$\lambda = \frac{h}{\sqrt{2m(E - V(x))}}$$

Time-Independent Schrodinger Equation

The classical equation for a 1D wave is

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$$

with solutions of the form

$$u(x, t) = \psi(x) \cos(\omega t),$$

where $\omega = 2\pi v = \frac{2\pi v}{\lambda}$. This gives us

$$\frac{d^2 \psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} \psi(x) = 0$$

Time-Independent Schrodinger Equation

Plugging in

$$\lambda = \frac{\hbar}{\sqrt{2m(E - V(x))}}$$

into

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

yields (after rearrangement)

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

where $\hbar = \frac{\hbar}{2\pi}$. This is the time-independent Schrödinger equation for a 1D quantum particle.

Quantum Harmonic Oscillator

The Schrödinger equation for the 1D quantum mechanical harmonic oscillator between masses m_1 and m_2 is

$$-\frac{\hbar}{2\mu} \frac{d\Psi_\nu(x)}{dx^2} + \frac{1}{2}kx^2\psi_\nu(x) = E_\nu\psi_\nu(x)$$

- $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the system.
- $k = \frac{d^2 V(x)}{dx^2} \Big|_{x=x_0}$ is the spring constant, which is just the curvature of the potential energy surface at the well minimum.

Quantum Harmonic Oscillator

The energies of the Harmonic oscillator are quantized,

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right); \quad \nu = 0, 1, 2, 3\dots$$

where

$$\omega = \sqrt{\frac{k}{\mu}}$$

is the angular frequency of oscillation. Notice that the frequencies are quantized. They are proportional to:

- The square root of the spring constant.
- The square root of the inverse of the reduced mass. Larger masses result in slower/lower energy frequencies.

Also note that larger masses lower both the zero point vibrational energy and the energy level spacing. Larger masses and smaller local curvature both cause the HO to act more classical!

Debye Model of a Crystal

Debye's model for a harmonic crystal defines the total vibrational energy of the crystal as

$$\bar{E} = \int_0^{\infty} d\omega g(\omega)(\hbar\omega) \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right)$$

where

$$n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

is the Bose occupation number and

$$g(\omega) = N \left(\frac{12\pi\omega^2}{(2\pi)^3 n V^3} \right)$$

is the density of states. The total number of oscillation modes with frequencies between ω and $\omega + d\omega$ is just $g(\omega)d\omega$.

MD Equations of Motion: Verlet Algorithm

Definition of the Taylor expansion of function $f(x)$ about $x = a$

$$f(x) \approx f(a) + \frac{f'(a)}{1!}(x - a) + \frac{f''(a)}{2!}(x - a)^2 + \mathcal{O}(x^3).$$

Apply a Taylor series expansion (with respect to time) up to second order for the position \mathbf{r}_i of a particle i centered about time t

$$\mathbf{r}_i(\tau) \approx \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)(\tau - t) + \frac{1}{2}\ddot{\mathbf{r}}_i(t)(\tau - t)^2.$$

At $\tau = t + \Delta t$ this becomes

$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}_i(t)\Delta t^2.$$

MD Equations of Motion: Verlet Algorithm

Similarly

$$\mathbf{r}_i(t - \Delta t) \approx \mathbf{r}_i(t) - \dot{\mathbf{r}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}_i(t)\Delta t^2.$$

Adding these two equations together (after rearrangement) yields

$$\mathbf{r}_i(t + \Delta t) \approx 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \ddot{\mathbf{r}}_i(t)\Delta t^2.$$

Then we can just plug in

$$\ddot{\mathbf{r}}_i(t) = \frac{\mathbf{F}_i(t)}{m_i}$$

to get the final equation of motion for the Verlet Algorithm:

$$\mathbf{r}_i(t + \Delta t) \approx 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m_i}\Delta t^2.$$

Sampling a Boltzmann Distribution

Not necessarily required for MD, as Boltzmann distribution will quickly develop. A Maxwell-Boltzmann distribution has the form

$$f(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2k_B T}}$$

The cumulative probability that a randomly chosen variable lies on the interval $v_x \in (-\infty, X]$ for some upper limit X is

$$P(X) = \int_{-\infty}^X dv_x f(v_x).$$

Notice that $P(X)$ is a number between 0 and 1.

Sampling a Boltzmann Distribution

If we choose uniformly distributed pseudo-random numbers ξ_1, \dots, ξ_{3N} and solve

$$P(X_i) = \xi_i$$

for X_i , and assign $v_{\alpha,i} = X_i$ for each particle i and component α , the resulting velocities will have been properly sampled from a Boltzmann distribution. Note that this method so far has not guaranteed that the center-of-mass velocity is zero. Usually the velocities are corrected to ensure there is no net drift of the system in time.

For example, the total drift of momentum in the x direction can be quickly calculated, then divided by the number of particles and the result subtracted from each particle.

Van der Waals Equation of State

The van der Waals equation of state for a non-ideal gas is

$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT.$$

or, in terms of the molar volume $V_m = \frac{V}{n}$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}.$$

a is a parameter related to the attractive interactions between molecules, and acts to reduce the pressure.

b is the excluded volume per mole, due to repulsive short-range interactions between molecules. In the hard sphere model, b is four times as large as the volume of the hard spheres themselves.

Claperyron Equation

Describes the slope of phase boundaries in a phase diagram for a single-component system. Along a phase boundary between phases α and β

$$d\mu(\alpha) = d\mu(\beta).$$

For a single component system

$$d\mu = -S_m dT + V_m dP$$

for both phases. Setting them equal leads to

$$\frac{dP}{dT} = \frac{\Delta S_{Transition}}{\Delta V_{Transition}}.$$