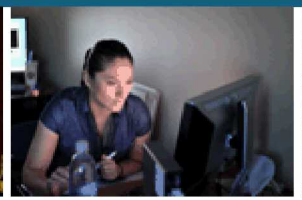
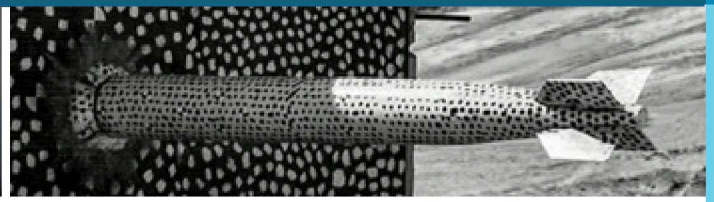
SAND2019-14710PE

Introduction to *Ab Initio* Equations of State





Raymond Clay

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Desired Quantities

- Equation of state: $E(\rho, T)$, $P(\rho, T)$
- Opacities
- Transport Coefficients

Properties over Large P-T Space

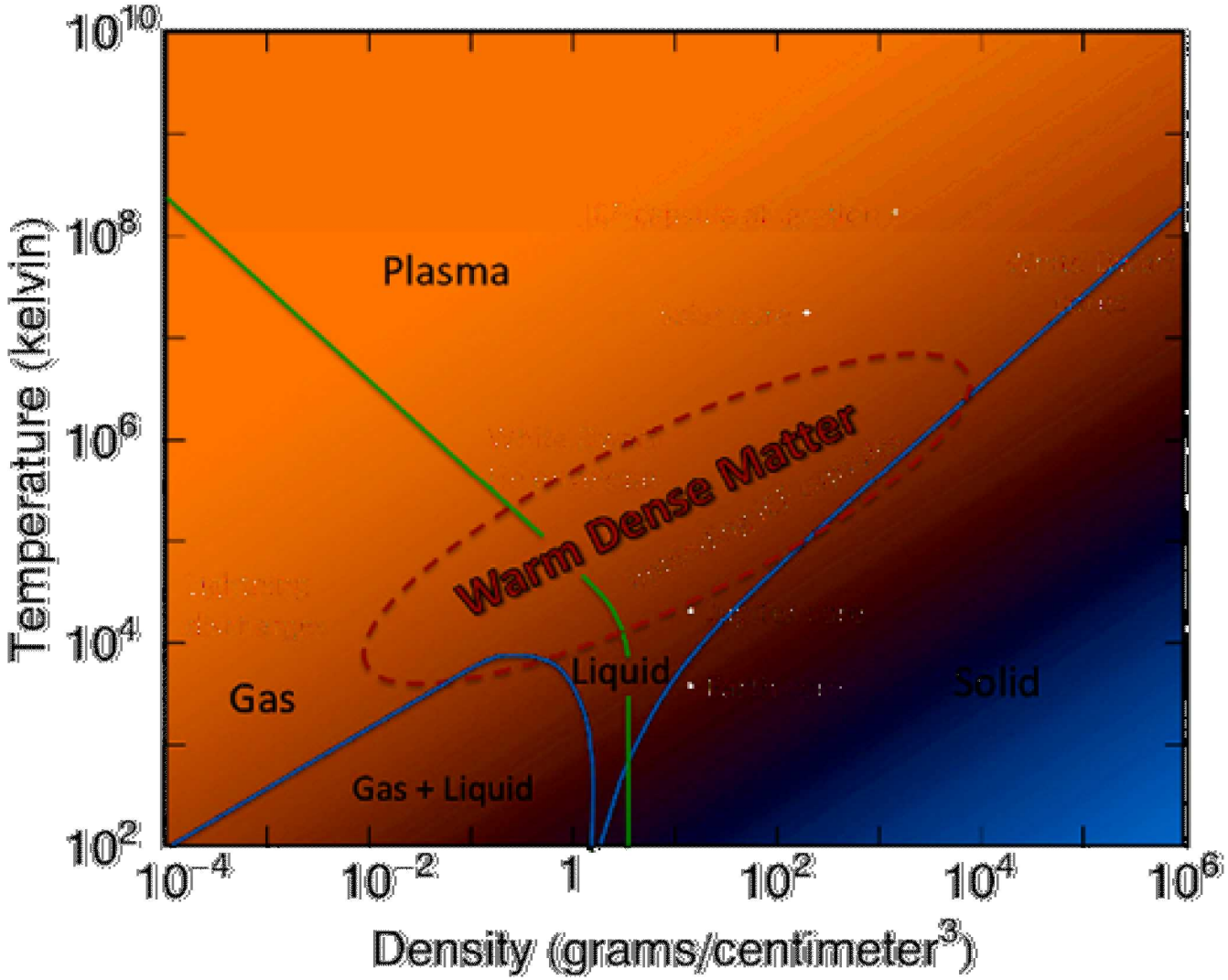


Figure from Mike Desjarlais

Theoretical Physics In a Nutshell

Exercise 1.1.1.1.1a: Given locality, causality, Lorentz invariance, and known physical data since 1860, show that the Lagrangian describing all observed physical processes (sans gravity) can be written:

$$\mathcal{L} = -\tfrac{1}{2}\partial_\nu g^a_\mu \partial_\nu g^a_\mu - g_s f^{abc}\partial_\mu g^a_\nu g^b_\mu g^c_\nu - \tfrac{1}{4}g_s^2 f^{abc}f^{ade}g^b_\mu g^c_\nu g^d_\mu g^e_\nu + \tfrac{1}{2}ig_s^2(\bar{q}^\sigma_i\gamma^\mu q^\sigma_j)g^a_\mu + \bar{G}^a\partial^2 G^a + g_s f^{abc}\partial_\mu \bar{G}^a G^b g^c_\mu - \partial_\nu W^+_\mu \partial_\nu W^-_\mu - M^2 W^+_\mu W^-_\mu - \tfrac{1}{2}\partial_\nu Z^0_\mu \partial_\nu Z^0_\mu - \tfrac{1}{2c_w^2}M^2 Z^0_\mu Z^0_\mu - \tfrac{1}{2}\partial_\mu A_\nu \partial_\mu A_\nu - \tfrac{1}{2}\partial_\mu H\partial_\mu H - \tfrac{1}{2}m_h^2 H^2 - \partial_\mu\phi^+\partial_\mu\phi^- - M^2\phi^+\phi^- - \tfrac{1}{2}\partial_\mu\phi^0\partial_\mu\phi^0 - \tfrac{1}{2c_w^2}M\phi^0\phi^0 - \beta_h[\tfrac{2M^2}{g^2} + \tfrac{2M}{g}H + \tfrac{1}{2}(H^2+\phi^0\phi^0+2\phi^+\phi^-)] + \tfrac{2M^4}{g^2}\alpha_h - igc_w[\partial_\nu Z^0_\mu(W^+_\mu W^-_\nu - W^+_\nu W^-_\mu) - Z^0_\nu(W^+_\mu\partial_\nu W^-_\mu - W^-_\mu\partial_\nu W^+_\mu) + Z^0_\mu(W^+_\nu\partial_\nu W^-_\mu - W^-_\nu\partial_\nu W^+_\mu)] - igs_w[\partial_\nu A_\mu(W^+_\mu W^-_\nu - W^+_\nu W^-_\mu) - A_\nu(W^+_\mu\partial_\nu W^-_\mu - W^-_\mu\partial_\nu W^+_\mu) + A_\mu(W^+_\nu\partial_\nu W^-_\mu - W^-_\nu\partial_\nu W^+_\mu)] - \tfrac{1}{2}g^2 W^+_\mu W^-_\mu W^+_\nu W^-_\nu + \tfrac{1}{2}g^2 W^+_\mu W^-_\nu W^+_\mu W^-_\nu + g^2c_w^2(Z^0_\mu W^+_\mu Z^0_\nu W^-_\nu - Z^0_\mu Z^0_\mu W^+_\nu W^-_\nu) + g^2 s_w^2(A_\mu W^+_\mu A_\nu W^-_\nu - A_\mu A_\mu W^+_\nu W^-_\nu) + g^2 s_w c_w[A_\mu Z^0_\nu(W^+_\mu W^-_\nu - W^+_\nu W^-_\mu) - 2A_\mu Z^0_\mu W^+_\nu W^-_\nu] - g\alpha[H^3 + H\phi^0\phi^0 + 2H\phi^+\phi^-] - \tfrac{1}{8}g^2\alpha_h[H^4 + (\phi^0)^4 + 4(\phi^+\phi^-)^2 + 4(\phi^0)^2\phi^+\phi^- + 4H^2\phi^+\phi^- + 2(\phi^0)^2H^2] - gMW^+_\mu W^-_\mu H - \tfrac{1}{2}g\tfrac{M}{c_w^2}Z^0_\mu Z^0_\mu H - \tfrac{1}{2}ig[W^+_\mu(\phi^0\partial_\mu\phi^- - \phi^-\partial_\mu\phi^0) - W^-_\mu(\phi^0\partial_\mu\phi^+ - \phi^+\partial_\mu\phi^0)] + \tfrac{1}{2}g[W^+_\mu(H\partial_\mu\phi^- - \phi^-\partial_\mu H) - W^-_\mu(H\partial_\mu\phi^+ - \phi^+\partial_\mu H)] + \tfrac{1}{2}g\tfrac{1}{c_w}(Z^0_\mu(H\partial_\mu\phi^0 - \phi^0\partial_\mu H) - ig\tfrac{s_w^2}{c_w}MZ^0_\mu(W^+_\mu\phi^- - W^-_\mu\phi^+) + igs_wMA_\mu(W^+_\mu\phi^- - W^-_\mu\phi^+) - ig\tfrac{1-2c_w^2}{2c_w}Z^0_\mu(\phi^+\partial_\mu\phi^- - \phi^-\partial_\mu\phi^+) + igs_wA_\mu(\phi^+\partial_\mu\phi^- - \phi^-\partial_\mu\phi^+) - \tfrac{1}{4}g^2W^+_\mu W^-_\mu[H^2 + (\phi^0)^2 + 2\phi^+\phi^-] - \tfrac{1}{4}g^2\tfrac{1}{c_w^2}Z^0_\mu Z^0_\mu[H^2 + (\phi^0)^2 + 2(2s_w^2-1)^2\phi^+\phi^-] - \tfrac{1}{2}g^2\tfrac{s_w^2}{c_w}Z^0_\mu\phi^0(W^+_\mu\phi^- + W^-_\mu\phi^+) - \tfrac{1}{2}ig^2\tfrac{s_w^2}{c_w}Z^0_\mu H(W^+_\mu\phi^- - W^-_\mu\phi^+) + \tfrac{1}{2}g^2s_wA_\mu\phi^0(W^+_\mu\phi^- + W^-_\mu\phi^+) + \tfrac{1}{2}ig^2s_wA_\mu H(W^+_\mu\phi^- - W^-_\mu\phi^+) - g^2\tfrac{s_w}{c_w}(2c_w^2-1)Z^0_\mu A_\mu\phi^+\phi^- - g^1s_w^2A_\mu A_\mu\phi^+\phi^- - \bar{e}^\lambda(\gamma\partial + m^\lambda_e)e^\lambda - \bar{\nu}^\lambda\gamma\partial\nu^\lambda - \bar{u}^\lambda_j(\gamma\partial + m^\lambda_u)u^\lambda_j - \bar{d}^\lambda_j(\gamma\partial + m^\lambda_d)d^\lambda_j + igs_wA_\mu[-(\bar{e}^\lambda\gamma^\mu e^\lambda) + \tfrac{2}{3}(\bar{u}^\lambda_j\gamma^\mu u^\lambda_j) - \tfrac{1}{3}(\bar{d}^\lambda_j\gamma^\mu d^\lambda_j)] + \tfrac{ig}{4c_w}Z^0_\mu[(\bar{\nu}^\lambda\gamma^\mu(1+\gamma^5)\nu^\lambda) + (\bar{e}^\lambda\gamma^\mu(4s_w^2 - 1 - \gamma^5)e^\lambda) + (\bar{u}^\lambda_j\gamma^\mu(\tfrac{4}{3}s_w^2 - 1 - \gamma^5)u^\lambda_j) + (\bar{d}^\lambda_j\gamma^\mu(1 - \tfrac{8}{3}s_w^2 - \gamma^5)d^\lambda_j)] + \tfrac{ig}{2\sqrt{2}}W^+_\mu[(\bar{\nu}^\lambda\gamma^\mu(1+\gamma^5)e^\lambda) + (\bar{u}^\lambda_j\gamma^\mu(1+\gamma^5)C_{\lambda\kappa}d^\kappa_j)] + \tfrac{ig}{2\sqrt{2}}W^-_\mu[(\bar{e}^\lambda\gamma^\mu(1+\gamma^5)\nu^\lambda) + (\bar{d}^\kappa_j C^\dagger_{\lambda\kappa}\gamma^\mu(1+\gamma^5)u^\lambda_j)] + \tfrac{ig}{2\sqrt{2}}\tfrac{m^\lambda_e}{M}[-\phi^+(\bar{\nu}^\lambda(1-\gamma^5)e^\lambda) + \phi^-(\bar{e}^\lambda(1+\gamma^5)\nu^\lambda)] - \tfrac{g}{2}\tfrac{m^\lambda_e}{M}[H(\bar{e}^\lambda e^\lambda) + i\phi^0(\bar{e}^\lambda\gamma^5 e^\lambda)] + \tfrac{ig}{2M\sqrt{2}}\phi^+[-m^\kappa_d(\bar{u}^\lambda_j C_{\lambda\kappa}(1-\gamma^5)d^\kappa_j) + m^\lambda_u(\bar{u}^\lambda_j C_{\lambda\kappa}(1+\gamma^5)d^\kappa_j] + \tfrac{ig}{2M\sqrt{2}}\phi^-[m^\lambda_d(\bar{d}^\lambda_j C^\dagger_{\lambda\kappa}(1+\gamma^5)u^\kappa_j) - m^\kappa_u(\bar{d}^\lambda_j C^\dagger_{\lambda\kappa}(1-\gamma^5)u^\kappa_j] - \tfrac{g}{2}\tfrac{m^\lambda_u}{M}H(\bar{u}^\lambda_j u^\lambda_j) - \tfrac{g}{2}\tfrac{m^\lambda_d}{M}H(\bar{d}^\lambda_j d^\lambda_j) + \tfrac{ig}{2}\tfrac{m^\lambda_u}{M}\phi^0(\bar{u}^\lambda_j\gamma^5 u^\lambda_j) - \tfrac{ig}{2}\tfrac{m^\lambda_d}{M}\phi^0(\bar{d}^\lambda_j\gamma^5 d^\lambda_j) + \bar{X}^+(\partial^2 - M^2)X^+ + \bar{X}^-(\partial^2 - M^2)X^- + \bar{X}^0(\partial^2 - \tfrac{M^2}{c_w^2})X^0 + \bar{Y}\partial^2 Y + igc_wW^+_\mu(\partial_\mu\bar{X}^0X^- - \partial_\mu\bar{X}^+X^0) + igs_wW^+_\mu(\partial_\mu\bar{Y}X^- - \partial_\mu\bar{X}^+Y) + igc_wW^-_\mu(\partial_\mu\bar{X}^-X^0 - \partial_\mu\bar{X}^0X^+) + igs_wW^-_\mu(\partial_\mu\bar{X}^-Y - \partial_\mu\bar{Y}X^+) + igc_wZ^0_\mu(\partial_\mu\bar{X}^+X^+ - \partial_\mu\bar{X}^-X^-) + igs_wA_\mu(\partial_\mu\bar{X}^+X^+ - \partial_\mu\bar{X}^-X^-) - \tfrac{1}{2}gM[\bar{X}^+X^+H + \bar{X}^-X^-H + \tfrac{1}{c_w^2}\bar{X}^0X^0H] + \tfrac{1-2c_w^2}{2c_w}igM[\bar{X}^+X^0\phi^+ - \bar{X}^-X^0\phi^-] + \tfrac{1}{2c_w}igM[\bar{X}^0X^-\phi^+ - \bar{X}^0X^+\phi^-] + igMs_w[\bar{X}^0X^-\phi^+ - \bar{X}^0X^+\phi^-] + \tfrac{1}{2}igM[\bar{X}^+X^+\phi^0 - \bar{X}^-X^-\phi^0]$$

Cascade of Approximations

$$\mathcal{L}^{QED} = \overline{\psi}\left(i\gamma^{\mu}\partial_{\mu} - m\right)\psi - J^{\mu}A_{\mu} - \tfrac{1}{4}F_{\mu\nu}F^{\mu\nu}$$

$$[\gamma^{\mu}(p_{\mu} - qA_{\mu}) - m]\psi = 0$$

Standard Model

Low energy. QCD doesn't matter.

QED

- Electric fields are classical
- Particle number is conserved (lose the fields)

Dirac Equation

- Non relativistic
- (Effective interactions)

$$i\partial_t \Psi = \hat{H}\Psi$$

$$\begin{aligned}
H &= T_n + H_{el} = T_n + T_e + V, \\
\hat{T}_n &= -\sum_{I=1}^{N_n} \lambda_I \hat{\nabla}_I^2, \quad \hat{T}_e = -\lambda_e \sum_{i=1}^{N_e} \hat{\nabla}_i^2, \\
\hat{V} &= \sum_{I<J} \frac{z_I z_J}{|\vec{R}_I - \vec{R}_J|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,I} \frac{z_I}{|\vec{r}_i - \vec{R}_I|}
\end{aligned}$$

Schrödinger Equation

Classical Mechanics

(Time-Independent) Schrödinger Equation

$$i\partial_t \Psi = \hat{H}\Psi \longrightarrow \hat{H}\Phi_N = E_N \Phi_N$$

Equilibrium properties fully determined.

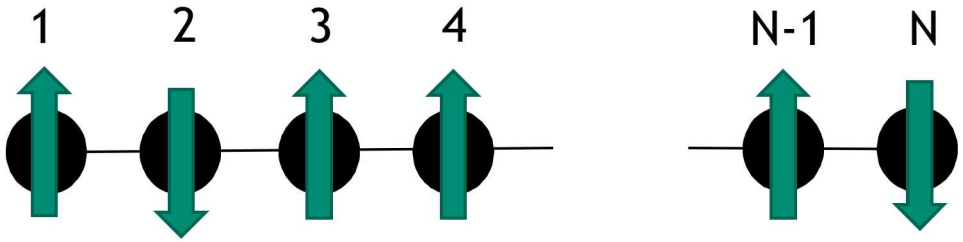
$$\mathcal{Z} = Tr(e^{-\beta \hat{H}}) = \sum_N e^{-\beta E_N} \longrightarrow F(\rho, T) = -kT \log(\mathcal{Z})$$

$$E(\rho, T) = -\frac{\partial}{\partial \beta}\mathcal{Z} \qquad P(\rho, T) = -\left(\frac{\partial F}{\partial V}\right)_T$$

Time-dependent properties within linear response regime:

- Electrical/Thermal Conductivity by Kubo-Greenwood
- Spectral functions, opacities, etc.

Solution of Schrödinger Equation…(Psych)



1) Build up basis states

$$|i\rangle = |\uparrow\downarrow\uparrow\uparrow \ldots \uparrow\downarrow\rangle$$

2) Write Hamiltonian in basis:

$$H_{ij} = \langle i|\hat{H}|j\rangle \qquad |\Phi\rangle = \sum_i c_i|i\rangle$$

3) Solve the eigen problem.

$$\mathbf{Hc} = E_N\mathbf{c}$$

Problems:

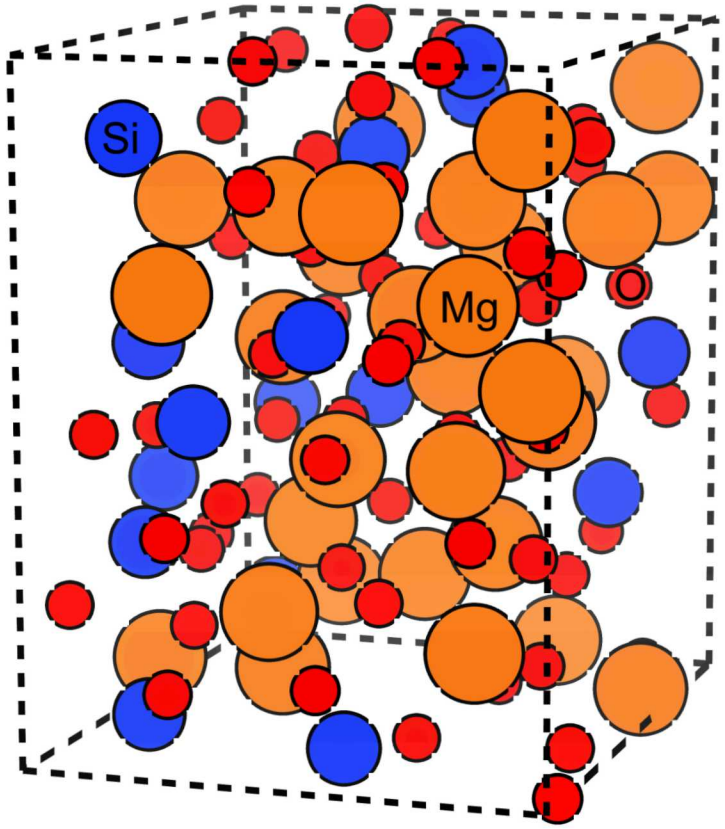
- **Dimensionality:**
  - 2^N basis functions.
  - Can store **c** for 39 spins in 64GB
- **Scaling:**
  - $O(2^N)$ memory cost, $O(2^{aN})$ computational cost. **EXPONENTIAL SCALING.**
  - Adding 1 spin doubles memory and multiplicatively increases computational cost.
- 3x3x3 spin block. What about $6.02\text{x}10^{23}$ electrons???

Plan of Attack by Atomistic Simulation

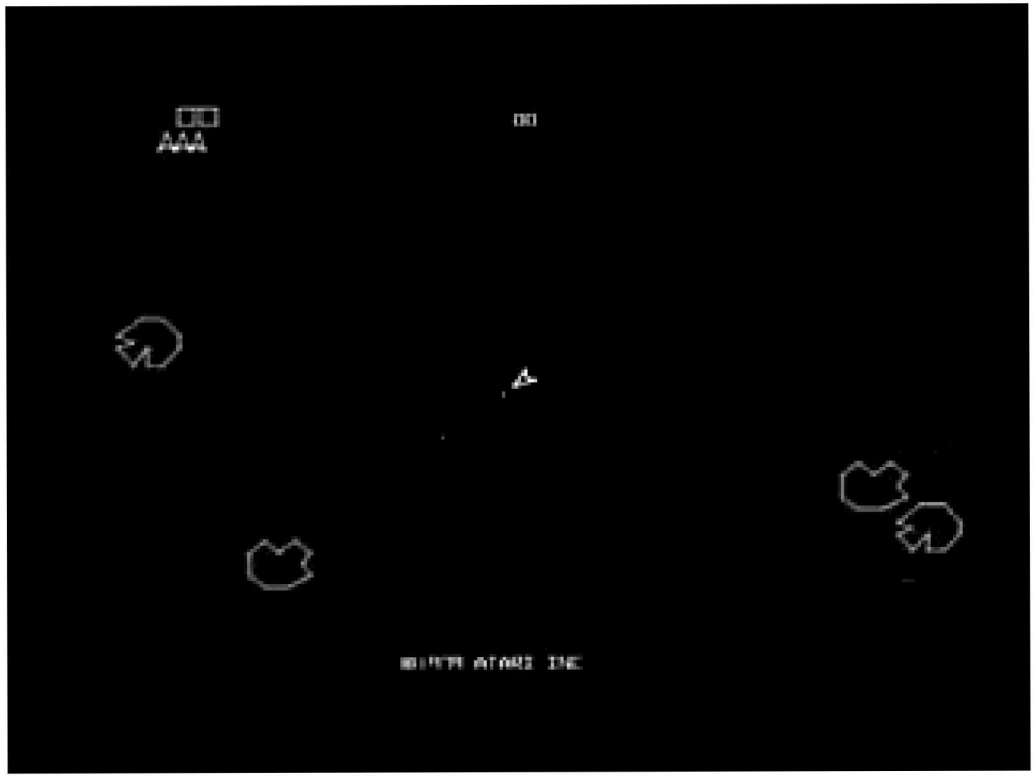
1. Consider a small system with N~100 ions and N~100 electrons.
2. Separate electronic and ionic degrees of freedom.
3. Solve the electronic problem. ☠
4. Solve the ionic problem.
5. **Extrapolate to the thermodynamic limit.**

Note: There are theories that are formulated in the thermodynamic limit. Not widely used in inhomogeneous systems.

Problem Statement: Mg_2SiO_4



1. We place N~100 ions and N~100 electrons in a box.
2. This defines the Hamiltonian by V(R) (nuclear charge & number of electrons.
3. Impose periodic boundary conditions.



Split Nuclei & Electrons: Born-Oppenheimer Approximation

Assume the wavefunction is separable.

$$\Psi_N(r, \mathbf{R}) = \Psi_N^{el}(\mathbf{r}; \mathbf{R})\chi_N^n(\mathbf{R})$$

We can approximately separate the electron and ion equations into the following equations:

$$\hat{H}^{el} = \hat{T}^{el} + \hat{V}_{eI}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{II}(\mathbf{R})$$

$$\hat{H}^{el}\Psi_N^{el}(\mathbf{r}; \mathbf{R}) = E_N^{el}(\mathbf{R})\Psi_N^{el}(\mathbf{r}; \mathbf{R})$$

$$(\hat{T}^n + E_N^{el}(\mathbf{R}))\chi_N^n(\mathbf{R}) = E_N\chi_N^n(\mathbf{R})$$

Well controlled approximation:

1. m/M is small
2. No near degeneracies between electronic energy levels.

$$E_0^{el}(\mathbf{R})$$

$$F^{el}(\mathbf{R}) = -kT\log(\mathcal{Z}^{el})$$

$$\mathcal{Z}^{el}(\mathbf{R}) = \sum_N e^{-\beta E_N^{el}(\mathbf{R})}$$

Solving the Ion Problem at Low Temperature

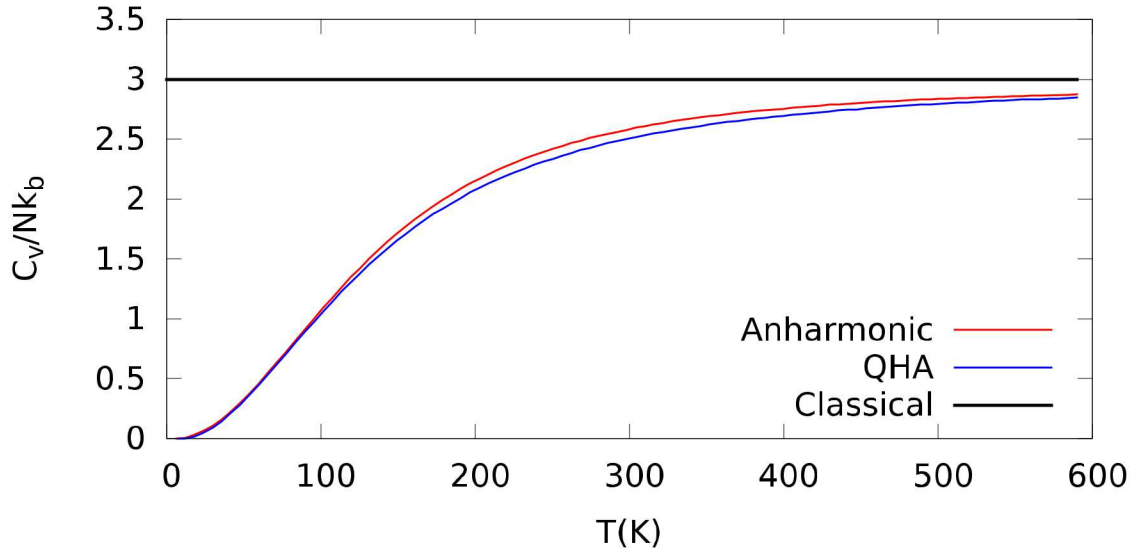
Quasi-harmonic Approximation

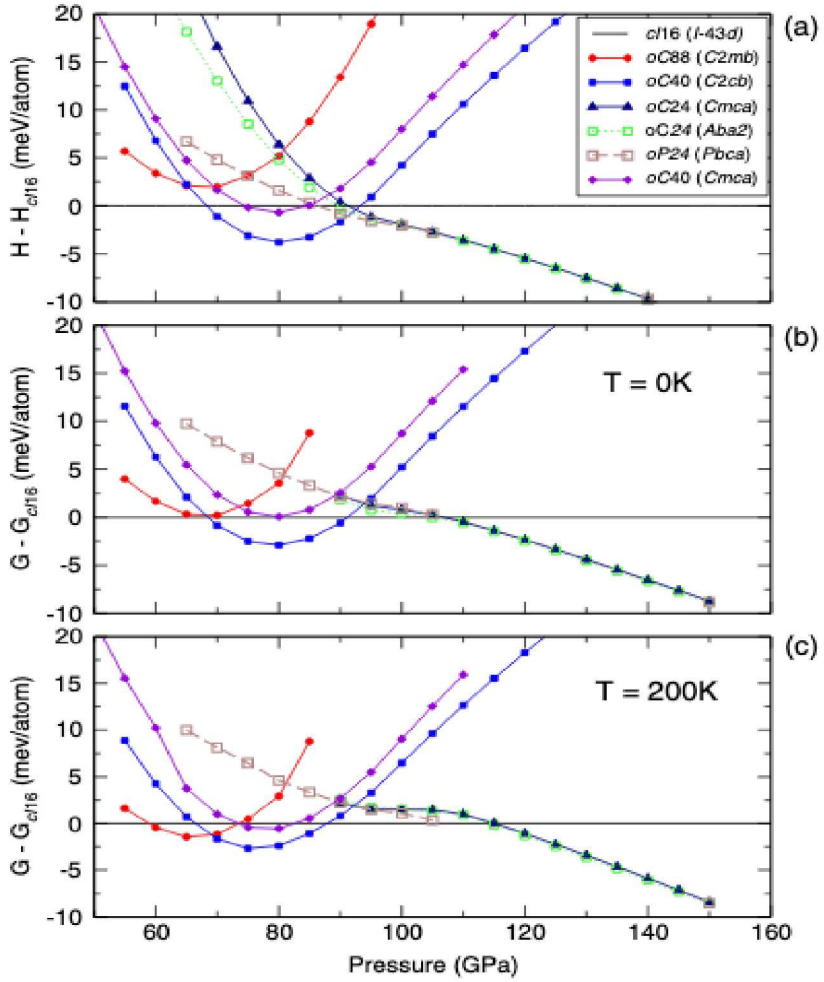
$$E^{el}(\mathbf{R}) \approx E^{el}(\mathbf{R}_0) + \frac{1}{2}(\mathbf{R}-\mathbf{R}_0)\cdot\nabla_{\mathbf{R}}\otimes\nabla_{\mathbf{R}}E^{el}\cdot(\mathbf{R}-\mathbf{R}_0)+\ldots$$

- Exactly diagonalize the nuclear Hamiltonian
- $F = E_0^{el} + F^{vib}$

Beyond Quasi-harmonic Approximation

- Keep more terms!





Solving the Ion Problem Everywhere Else: Molecular Dynamics

Assuming classical nuclei, we want to compute the following:

$$\langle A \rangle_\beta = \frac{1}{Z} \int d\mathbf{R} A(\mathbf{R}) \exp\left(-\beta F^{el}(\mathbf{R})\right)$$

$$Z = \int d\mathbf{R} \exp\left(-\beta F^{el}(\mathbf{R})\right)$$

Integrate classical equations of motion for ensemble at temperature T

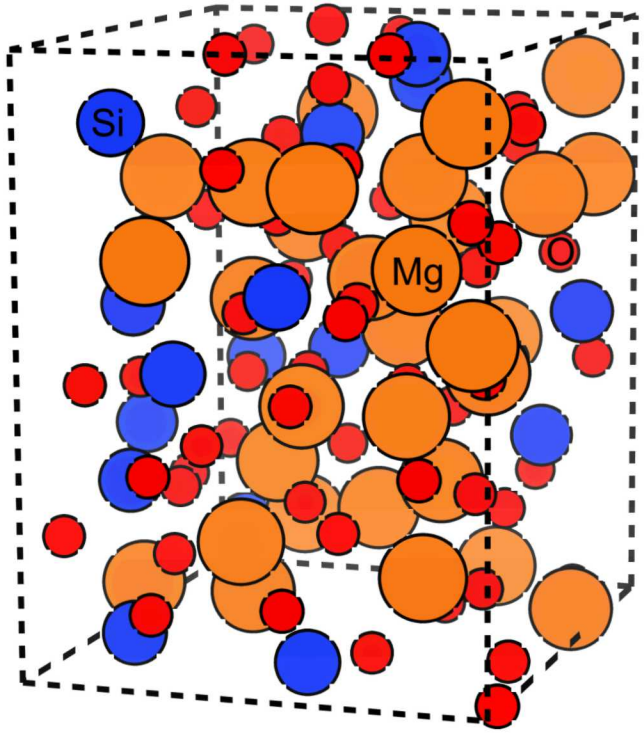
$$\dot{\mathbf{P}}(t) = -\nabla_{\mathbf{R}} F^{el}(\mathbf{R}) - \gamma \dot{\mathbf{R}}(t) - \sqrt{2M\gamma k_b T}\xi(t)$$

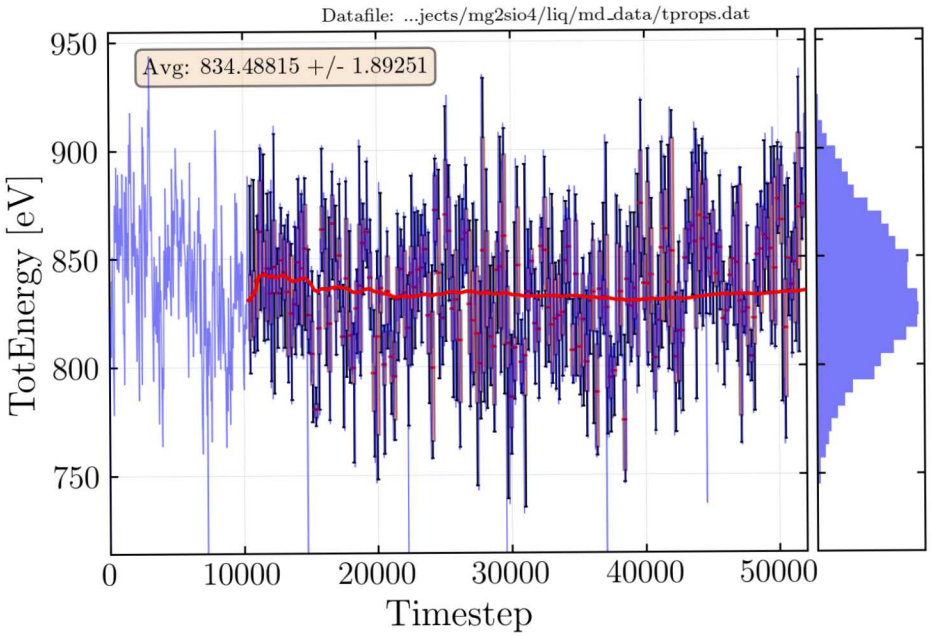
$$\langle A \rangle_\tau = \frac{1}{\tau} \int_0^\tau dt A(\mathbf{R}(t))$$

Ergodic Hypothesis

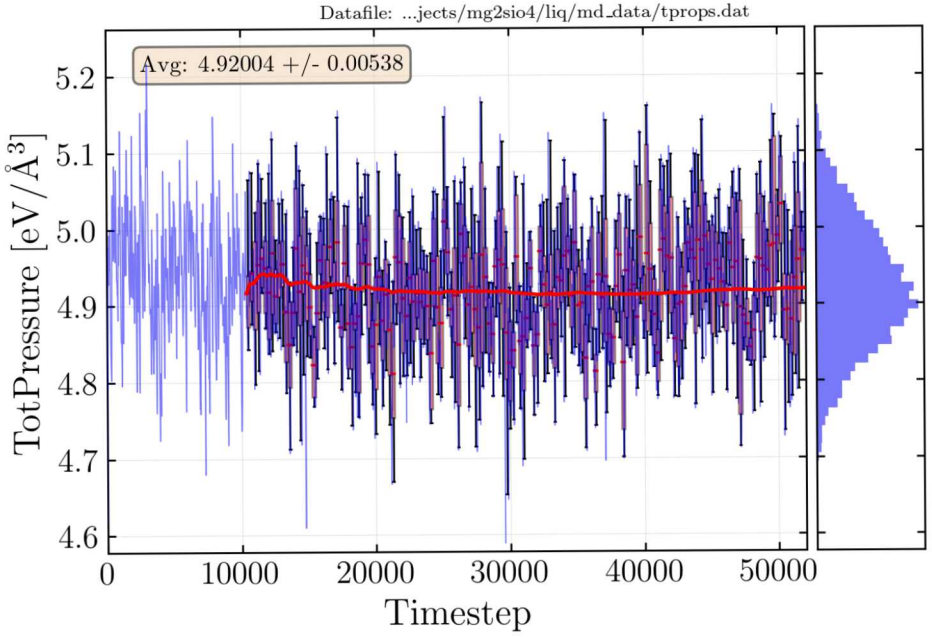
$$\langle A \rangle_\beta = \langle A \rangle_\tau$$

Example: Mg_2SiO_4





$\rightarrow E(\rho, T)$



$\rightarrow P(\rho, T)$

What can we compute?

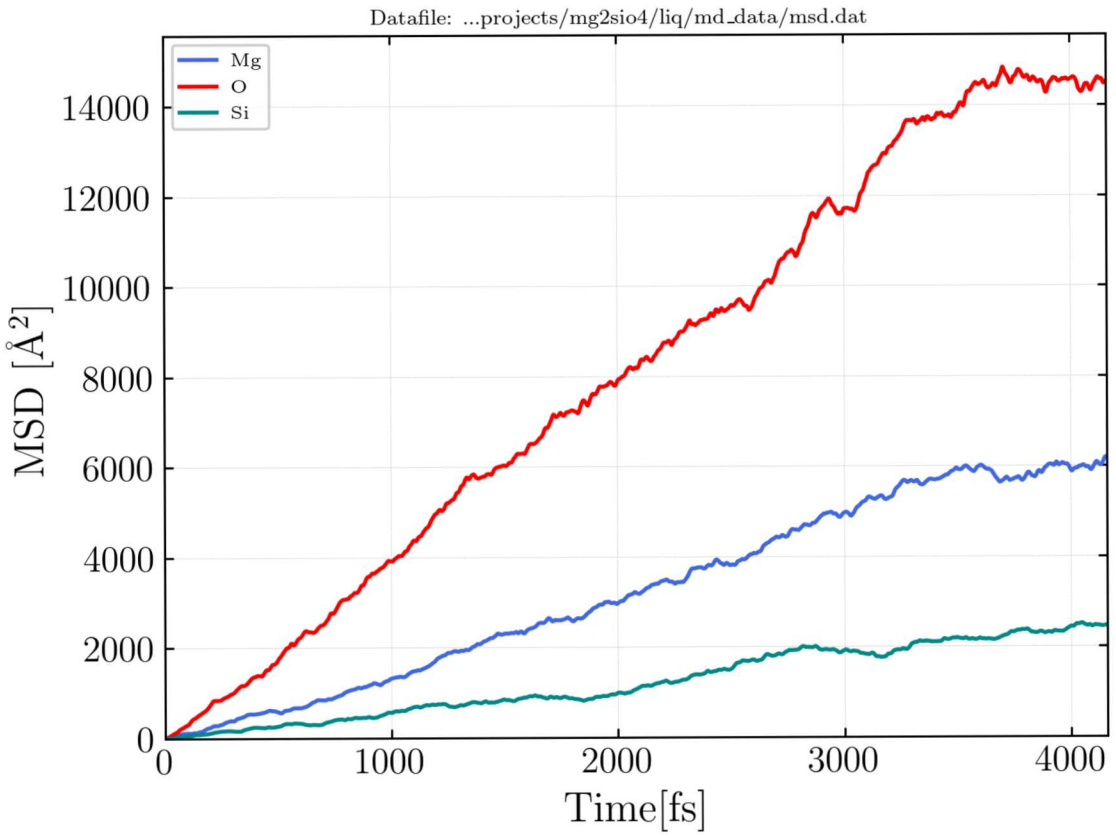
Electronic Properties

- Energies & Pressures
- Electrical conductivity
- Optical properties

Ionic Dynamical Properties

- Ionic diffusion constants
- VACF

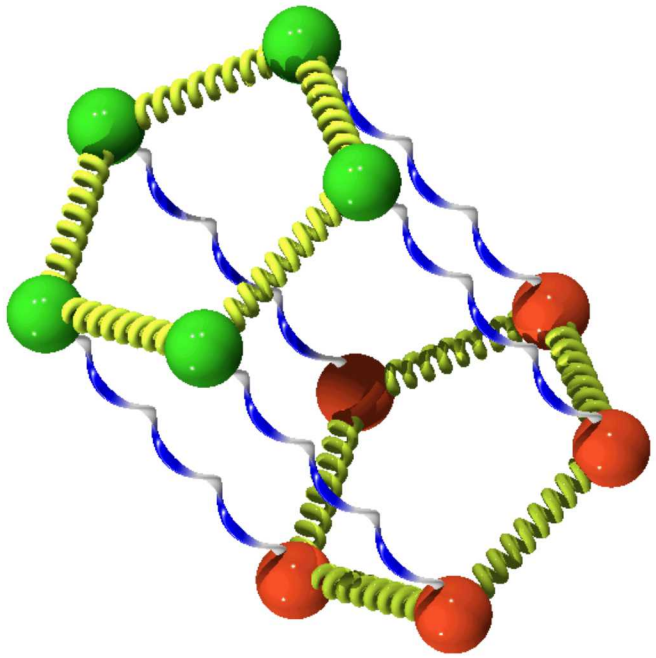
$$\langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle_\beta = 6 D_i t$$

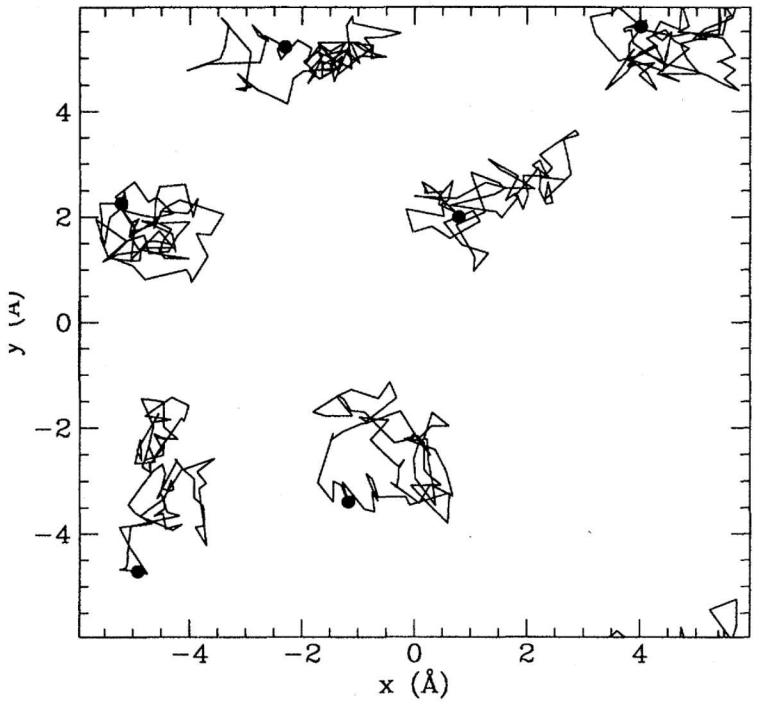


Solving the Ionic Problem: Final Thoughts

Quantum Nuclei at Finite Temperature

$$\mathcal{Z} = \int \mathcal{D}[\mathbf{R}] \exp\left(-\int_0^\beta dt \left[T(\mathbf{R}(t)) + F^{el}(\mathbf{R}(t)) \right] \right)$$





- Path-integral molecular dynamics
- Ring-Polymer Molecular Dynamics
- Path-integral Monte Carlo

Solving the Electronic Problem

$$\hat{H}^{el}\Psi_N^{el}(\mathbf{r};\mathbf{R}) = E_N^{el}(\mathbf{R})\Psi_N^{el}(\mathbf{r};\mathbf{R})$$

Method	Scaling	Ground State	Excited State	Free Energy
Full CI	Exp	◍	◍	◍
Hartree-Fock	$O(N^4)$	◍	◍	◍
Coupled Cluster	$O(N^6)$+	◍	◍	●
Kohn-Sham DFT	$O(N^3)$+	◍	●	◍
Orbital-Free DFT	O(N)	◍	●	◍
VMC/DMC	$O(N^3)$+	◍	◈	●
GW	$O(N^5)$	◍	◍	◍
RPIMC	$O(N^3)$	●	●	◍

Hohenberg-Kohn Theorem (Ground State)

- **Theorem 1:** *"The external potential V_{ext} is uniquely determined by the ground state density $\rho_0(\mathbf{r})$".*
- **Theorem 2:** *"There exists a functional of the density whose variational minimum corresponds to the ground state energy E_0 and density $\rho_0(\mathbf{r})$ of the true many-body system."*

$$E_{HK}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})V_{ext}(\mathbf{r}) + F[\rho]$$

- $\rho_0(\mathbf{r})$ is enough to determine everything knowable about the system.
- If we knew $E_{HK}[\rho]$ (which exists), we could find $\rho_0(\mathbf{r})$.

NOTE: Extensions of Hohenberg-Kohn can be done for a free-energy functional, for time-dependent functionals.

Density Functional Theory

$$\hat{H}^{el}\Psi_N^{el}(\mathbf{r};\mathbf{R}) = E_N^{el}(\mathbf{R})\Psi_N^{el}(\mathbf{r};\mathbf{R})$$

$$F[\rho] \quad \rho(\mathbf{r})$$

Kohn-Sham Density Functional Theory

KS-DFT is a method of approximating the universal exchange correlation functional. Ansatz is as follows:

$$E_{KS}[\rho] = T_{KS}[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})V_{ext}(\mathbf{r})$$

$$E_{Hartree}[\rho] = \int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

1) Decompose the density into a set of orthonormal orbitals: $\rho(\mathbf{r}) = \sum_{i=0}^{N-1} |\phi_i(\mathbf{r})|^2$

2) Evaluate the functional as follows: $T_{KS}[\rho] = -\frac{1}{2}\sum_{i=0}^{N-1} \int d\mathbf{r}\phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})$

$E_{xc}[\rho]$

Exchange-Correlation energy functional:
A.K.A. the “everything we missed” energy functional

Intuition for $E_{xc}[\rho]$

Exchange energy:

$$\Psi_{HF} = \det(M) \qquad M = \phi_j(\mathbf{r}_i)$$

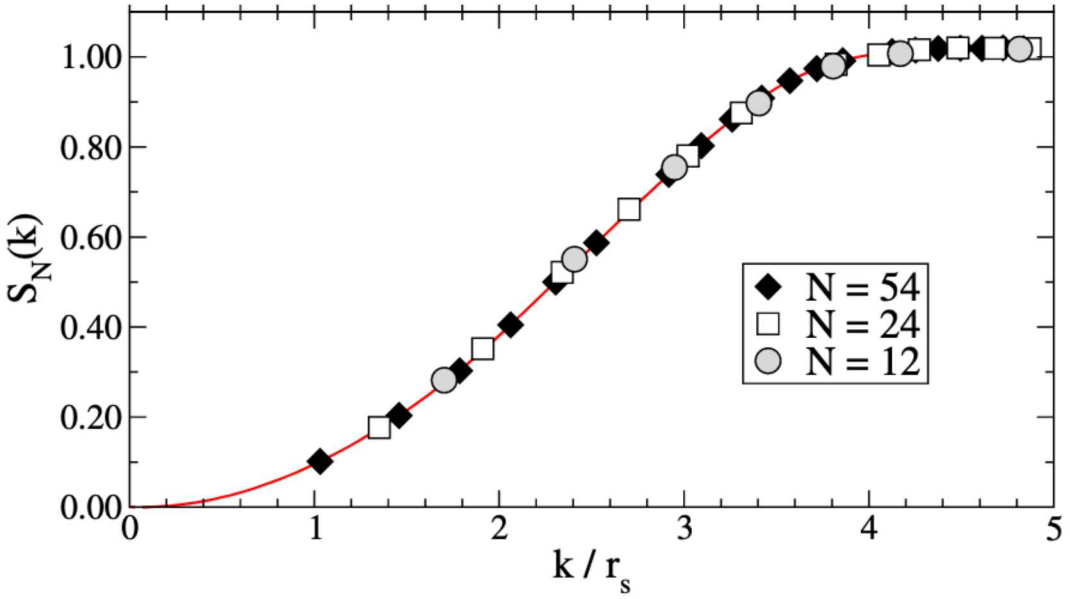
$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = T_{KS}[\rho] + E_{Hartree}[\rho] + E_x^{HF}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r})$$

$$E_x^{HF}[\rho] = -\sum_{i<j} \int d\mathbf{r} d\mathbf{r}' \frac{\phi_i^*(\mathbf{r}')\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Correlation energy:

$$g(\mathbf{r}) = \frac{1}{\rho} \langle \sum_{i \neq 0} \delta(\mathbf{r} - \mathbf{r}_i) \rangle \qquad S_N(\mathbf{k}) = \frac{1}{N} \langle \delta\rho_{\mathbf{k}} \delta\rho_{-\mathbf{k}} \rangle$$

$$\langle V_N \rangle = \frac{\rho}{2} \int_0^{r_c} d\mathbf{r} v_{sr}(r)[g_N(r) - 1] + \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} v_k^{lr}[S_N(k) - 1]$$



How do we approximate $E_{xc}[\rho]$

- Calculate exchange-correlation energy **exactly** for model systems.
- Try to satisfy exact constraints… usually analytic and based on model systems.

$e_{XC}(\rho,T)$ is known for the homogeneous electron gas

VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

Ground State of the Electron Gas by a Stochastic Method

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(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

PACS numbers: 67.90.+i, 71.45.Gm

Approximations!

Local Density Approximation: $$E_{xc}^{LDA} = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{xc}^{hom}(\rho(\mathbf{r}))$$

Generalized Gradient Approximation (GGA): $$E_{xc}^{GGA}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})F(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))\epsilon_{xc}^{hom}(\rho(\mathbf{r}))$$

Hybrid Functionals: $$E_x^{hybrid}[\rho] = (1-\alpha)E_x^{GGA}[\rho] + \alpha E_x^{HF}[\rho]$$

Non-local van der Waals: $$E_c^{nl}[\rho] = \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})K(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')$$

A small list from LibXC…

LDA: LDA, PW92, TETER93

GGA: AM05, BGCP, B97-GGA1, B97-K, BLYP, BP86, EDF1, GAM, HCTH-93, HCTH-120, HCTH-147, HCTH-407, HCTH-407P, HCTH-P14, PBEINT, HTBS, KT2, MOHLYP, MOHLYP2, MPBE, MPW, N12, OLYP, PBE, PBEINT, PBESOL, PW91, Q2D, SOGGA, SOGGA11, TH-FL, TH-FC, TH-FCFO, TH-FCO, TH1, TH2, TH3, TH4, XLYP, XPBE, HLE16

MetaGGA: M06-L, M11-L, MN12-L, MS0, MS1, MS2, MVS, PKZB, TPSS, HLE17

Hybrids: B1LYP, B1PW91, B1WC, B3LYP, B3LYP*, B3LYP5, B3LYP5, B3P86, B3PW91, B97, B97-1 B97-2, B97-3, BHANDH, BHANDHLYP, EDF2, MB3LYP-RC04, MPW1K, MPW1PW, MPW3LYP, MPW3PW, MPWLYP1M, O3LYP, OPBE, PBE0, PBE0-13, REVB3LYP, REVPBE, RPBE, SB98-1A, SB98-1B, SB98-1C, SB98-2A, SB98-2B, SB98-2C, SOGGA11-X, SSB, SSB-D, X3LYP

MetaHybrids: B86B95, B88B95, BB1K, M05, M05-2X, M06, M06-2X, M06-HF, M08-HX, M08-SO, MPW1B95, MPWB1K, MS2H, MVSH, PW6B95, PW86B95, PWB6K, REVTPSSH, TPSSH, X1B95, XB1K

Range-separated: CAM-B3LYP, CAMY-B3LYP, HJS-PBE, HJS-PBESOL, HJS-B97X, HSE03, HSE06, LRC_WPBE, LRC_WPBEH, LCY-BLYP, LCY-PBE, M11, MN12-SX, N12-SX, TUNED-CAM-B3LYP, WB97, WB97X

We've specified $E_{KS}[\rho]$ by picking $E_{XC}[\rho]$. How do we get the ground state energy and density?

The Kohn-Sham Equations

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$v_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}$$

- Introduce a basis.
- Use density to determine $v_{eff}(\mathbf{r})$. $\rho(\mathbf{r}) = \sum_{i=0}^{N-1} |\phi_i(\mathbf{r})|^2$
- Solve the eigenproblem.
- Update density to correspond to new set of orbitals.
- Repeat until density and orbitals stop changing.

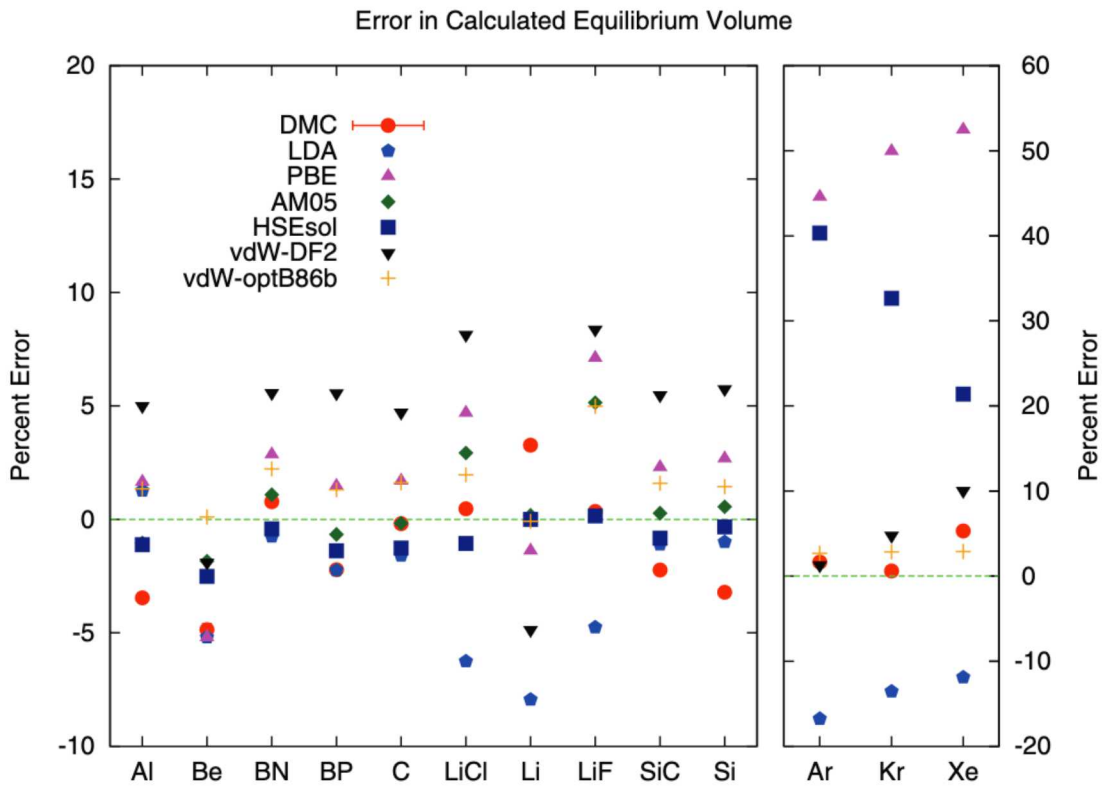
$O(N^3)$ for matrix diagonalization

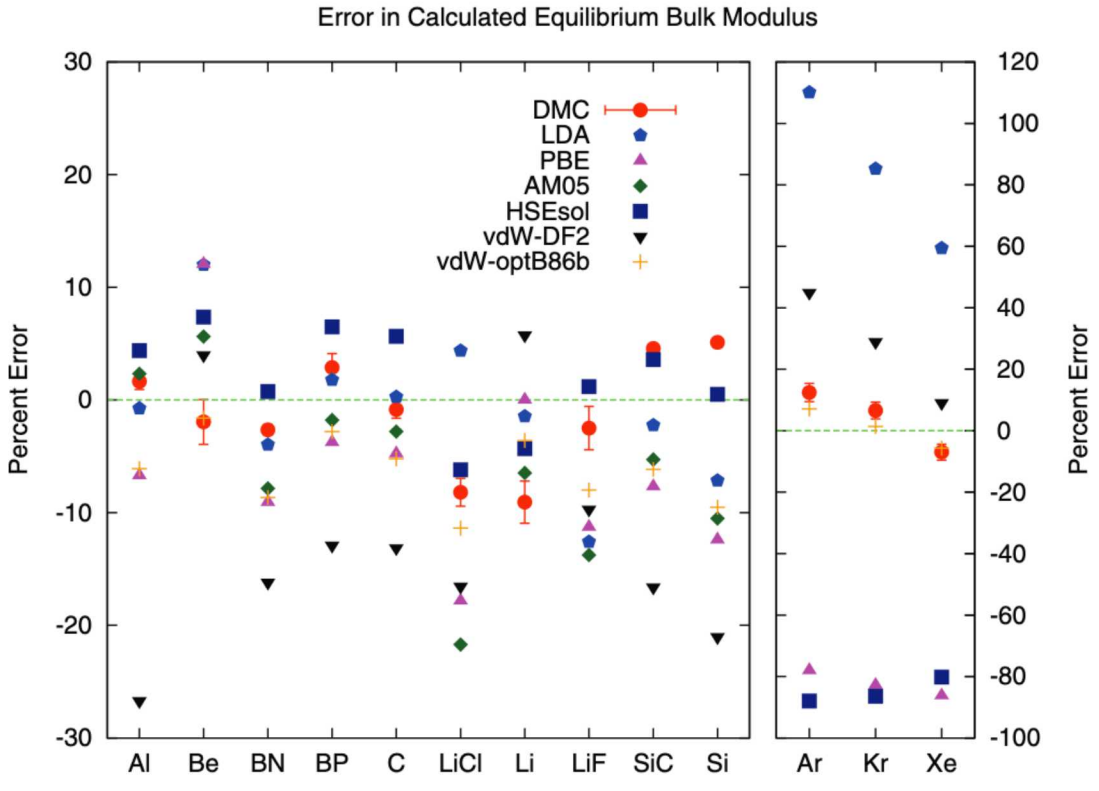
What is Computable within DFT?

$$E_0^{el}(\mathbf{R}) \qquad F^{el}(\mathbf{R}) = -kT\log(\mathcal{Z}^{el})$$

- **Ground-state energy, free energy.**
- **Specific heats.**
- **Pressures, forces, elastic constants.**
- **Electrical/thermal conductivities, optical properties.**
  - Computable within Kubo-Greenwood for the **auxiliary KS system**.
  - Good approximation most of the time.
  - Ground state KS serves as basis for rigorous many-body methods like QMC and GW.

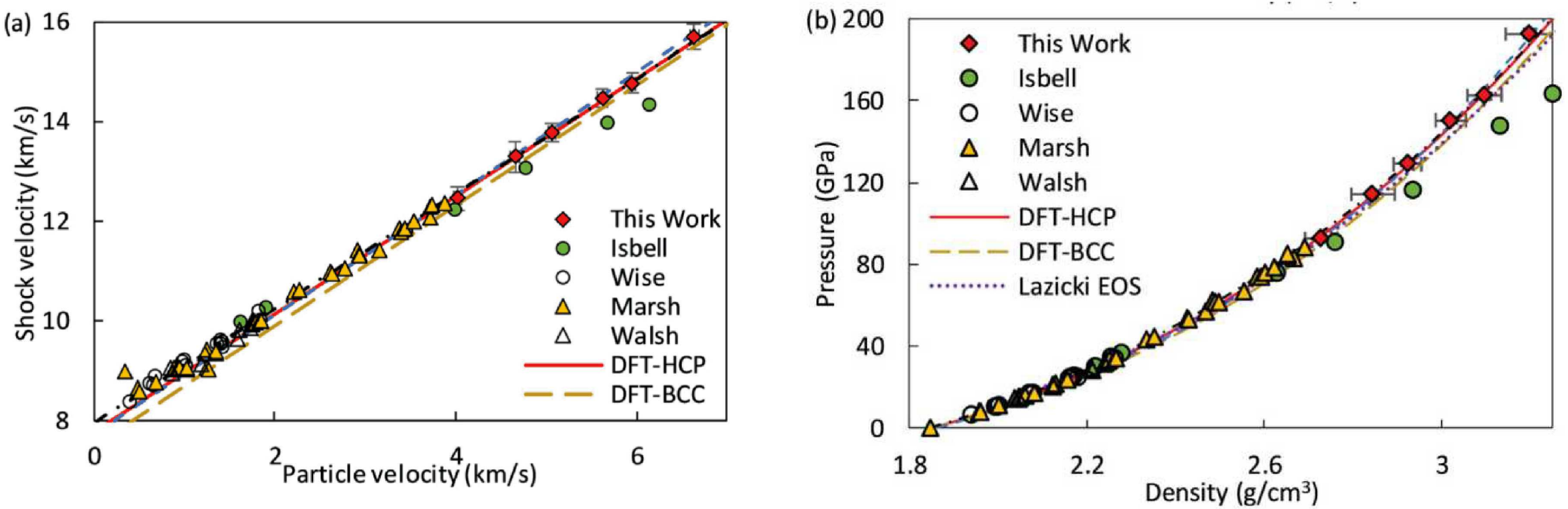
DFT In Practice: 0K Equation of State.





Shulenburger & Mattsson, PRB 88, 2013

Finite Temperature: Beryllium Hugoniot

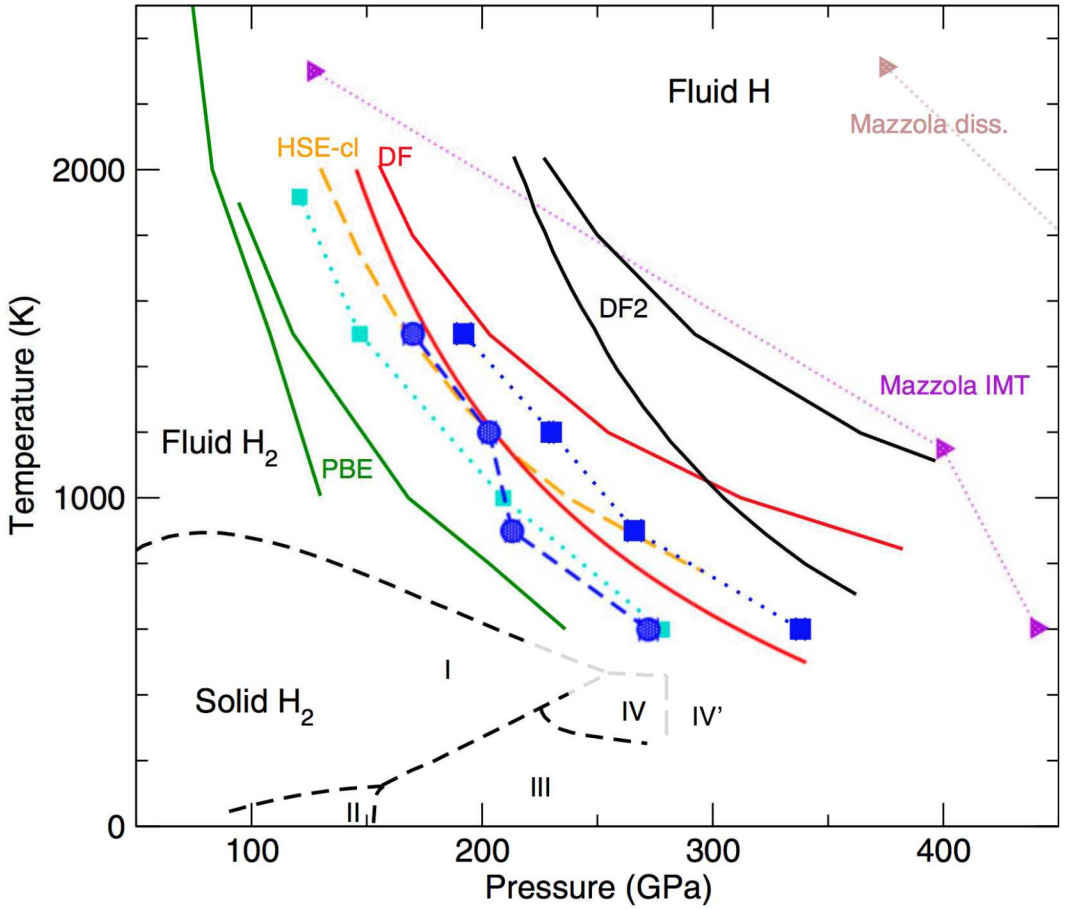


McCoy, Knudson, Desjarlais, PRB 100, 2019

Difficulties with DFT

1) Insulator-to-metal transitions. (self-interaction errors + band gap)
2) Molecular disassociation. (multireference issues + self-interaction errors)
3) Band-gaps. (derivative discontinuity)
4) Magnetic phase transitions. (energies are small)
5) Error cancellation.

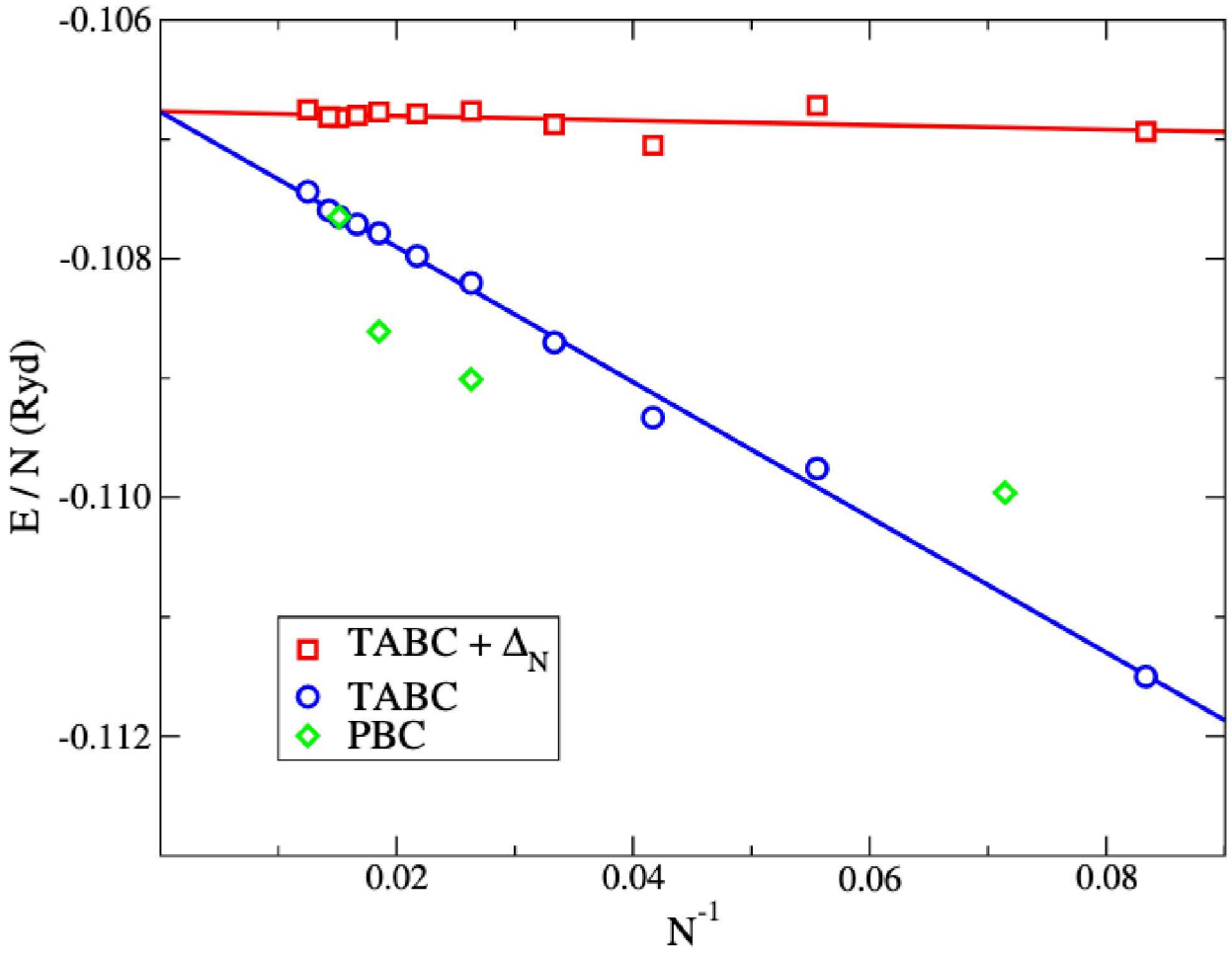
In parallel with DFT, many-body methods development occurs in 1641.



Pierleoni *et al.*, PNAS 113, 2016

Finite-Size Effects

- Need to be large enough to capture relevant correlations.
- After that, difference between thermodynamic limit and finite cells are often integration errors.
- Run multiple cell sizes, look how properties converge.



Chiesa *et al.* PRL 97, (1997)

Conclusions & Questions