UNIVERSITY of FLORIDA

The HIG of tdDFT

Sam Trickey

Quantum Theory Project
Physics, Chemistry - University of Florida

IPAM HEDP Long Program Tutorial
16 March 2012

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The Highly Important Games of Temperature-dependent DFT and Hartree-Fock

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Topics

- Motivation: Physics of Warm Dense Matter: see M. Desjarlais on 12 Mar. and F. Graziani on 13 Mar.
- Survey
    - Problems of naïve variational theory (Zero T, finite T)
    - Implications for molecular dynamics on complicated materials
    - Density functional theory basics – Zero T, finite T
    - Finite-T Hartree-Fock
    - Open questions for WDM applications

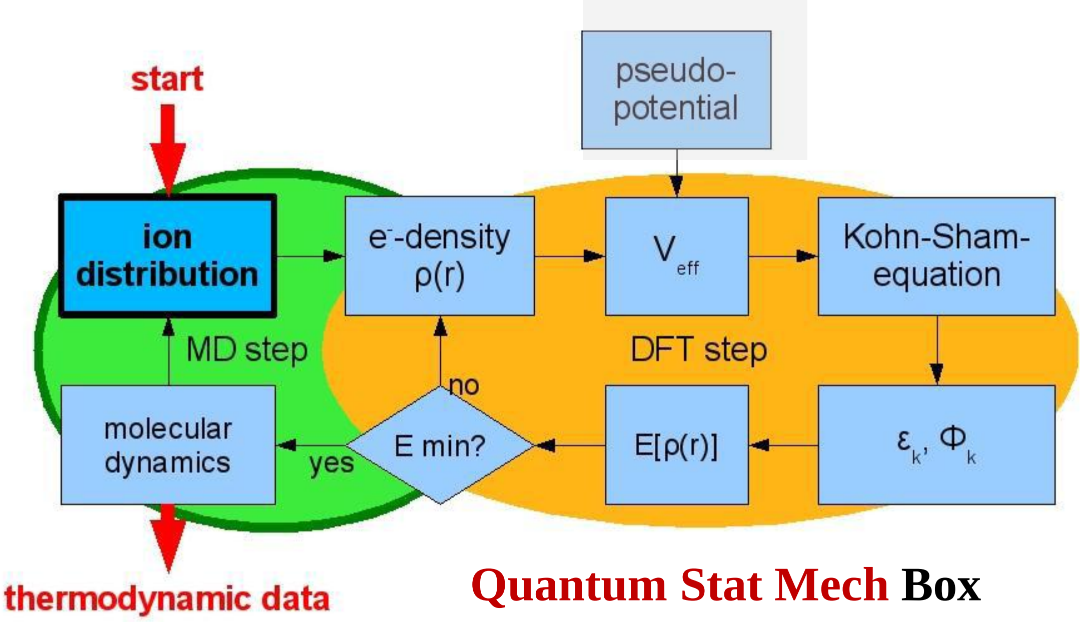
- Challenge: Orbital-free functionals
- Progress: New functionals, new reference calculations

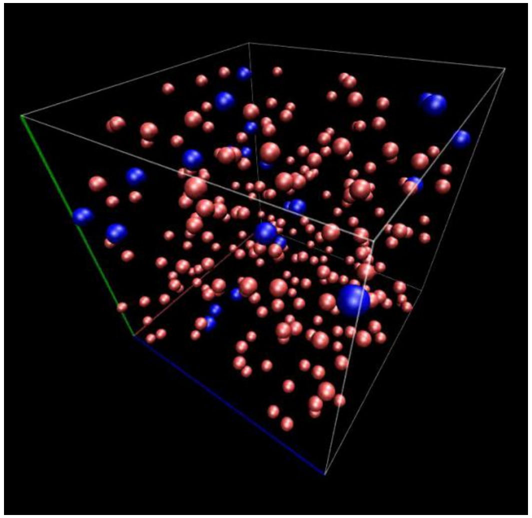
WDM Systems and Simulation Bottleneck

Molecular dynamics is a major simulation tool; See M. Murillo 14, 15 March.
MD implements Newton's 2nd Principle: $m_I \ddot{\mathbf{R}}_I = -\vec{\nabla}_I V(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$

Bottleneck: the potential. For electrons & ions, that should be the Born-Oppenheimer free- energy surface

$$V(\{\mathbf{R}\}) = \mathcal{F}(\{\mathbf{R}\}) + E_{ion-ion}(\{\mathbf{R}\})$$





H-He (8.6%) @ 1 Mbar, 4 kK

$\mathcal{F}(\{\mathbf{R}\})$ is the *electronic* free energy.
Quantum Stat Mech →
$ $ $ $ or € € € € €

Quantum Stat Mech Box
WDM: NO small parameters to do the QM!

Adapted from R. Redmer, LBNL WDM, 2011

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Many-electron Quantum Mechanics

- **The time-independent Schrödinger equation & Hamiltonian for the *N_e*-electron problem with *N* fixed nuclei (Hartree atomic units):**

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)\Psi_0\left(\mathbf{r}_1,\sigma_1,\ldots\mathbf{r}_{N_e},\sigma_{N_e};\{\mathbf{R}\}\right)=\mathcal{E}_{0;\{\mathbf{R}\}}\Psi_0\left(\mathbf{r}_1,\sigma_1,\ldots\mathbf{r}_{N_e},\sigma_{N_e};\{\mathbf{R}\}\right)$$

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)=-\tfrac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2-\sum_{i,I}^{N_e,N}\frac{Z_I}{\left|\mathbf{r}_i-\mathbf{R}_I\right|}+\tfrac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

$$:=\sum_{i=1}^{N_e}h\left(\mathbf{r}_i\right)+\tfrac{1}{2}\sum_{i\neq j}^{N_e}g\left(\mathbf{r}_i,\mathbf{r}_j\right)$$

Sum of 1- & 2-body Hamiltonians; symmetric on interchange of a pair

Nuclear (ion) positions (Born-Oppenheimer approx.); suppressed hereafter unless directly relevant.

***N_e* = number of electrons**
***N* = number of nuclei**

- **The many-electron wave function is anti-symmetric on interchange of a pair:**

$$\Psi_0\left(\mathbf{r}_1,\sigma_1,\ldots\mathbf{r}_k,\sigma_k\ldots\mathbf{r}_j,\sigma_j\ldots\mathbf{r}_{N_e},\sigma_{N_e};\{\mathbf{R}\}\right)=-\Psi_0\left(\mathbf{r}_1,\sigma_1,\ldots\mathbf{r}_j,\sigma_j\ldots\mathbf{r}_k,\sigma_k\ldots\mathbf{r}_{N_e},\sigma_{N_e};\{\mathbf{R}\}\right)$$

- **Hartree & traditional units:**

$$\hbar=m_{electron}=q_{electron}=1$$

$$1\,\mathrm{E}_{Hartree}=27.2116\ \mathrm{eV}\qquad 1\ \mathrm{au.}=0.5292\ \text{Å}$$

$$\text{One-electron KE:}-\tfrac{1}{2}\int d\mathbf{r}\,\phi\nabla^2\phi$$

- Rydberg & traditional units:

$$\hbar=2m_{electron}=q_{electron}/\sqrt{2}=1$$

$$1\,\mathrm{E}_{Rydberg}=13.6058\ \mathrm{eV}\qquad 1\ \mathrm{au.}=0.5292\ \text{Å}$$

$$\text{One-electron KE:}-\int d\mathbf{r}\,\phi\nabla^2\phi$$

Why many-electron problem is tough; T=0 K Variational Principle

The variational principle

$$\mathcal{E}_0 \le \mathcal{E}_{trial} = \frac{\int \Psi^*_{trial}\, \widehat{\mathcal{H}}\, \Psi_{trial}\, d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e}}{\int \Psi^*_{trial}\, \Psi_{trial}\, d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e}}$$

is equivalent to the Schrödinger equation. That is, the Schrödinger eqn. arises from requiring the first-order variation of $\mathcal{E}_{\mathbf{trial}}$ to be zero:

$$\delta\mathcal{E}_{trial} = \frac{\delta\mathcal{E}_{trial}}{\delta\Psi^*_{trial}}\,\delta\Psi^*_{trial} = 0$$

$$\int \delta\Psi^*_{trial}\,(\widehat{H} - \mathcal{E})\Psi_{trial}\, d\vec{r}_1 \ldots d\vec{r}_{N_e} = 0$$

$$\Rightarrow \widehat{H}\Psi_0 = \mathcal{E}_0\Psi_0$$

Lagrange Multiplier to preserve normalization

So why not just guess a trial wave function with a bunch of physically and chemically plausible parameters and do the minimization calculation by brute force numerical quadrature?

Examples, T=0 K Variational Principle

Approximate vs. exact wave functions:

$$\psi_{trial}\left(1,2,\ldots,N_e\right) \approx \mathcal{A}\left[\tilde{\varphi}_a\left(1\right)\tilde{\varphi}_b\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right]$$

HF is *approx*

↑Anti-symmetrizer

Full CI

$$\psi_{trial}\left(1,2,\ldots,N_e\right) = c_0\mathcal{A}\left[\tilde{\varphi}_a\left(1\right)\tilde{\varphi}_b\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right]$$

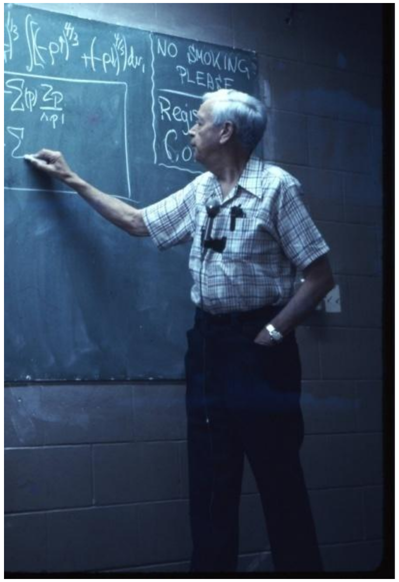
All “excited” Slater determinants

$$\left\{\begin{array}{l} +c_1\mathcal{A}\left[\tilde{\varphi}_A\left(1\right)\tilde{\varphi}_b\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right] \\ +c_2\mathcal{A}\left[\tilde{\varphi}_a\left(1\right)\tilde{\varphi}_B\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right] \\ +\ldots \end{array}\right.$$

Question 1: is this expansion exact? YES

Question 2: is this expansion rapidly converging? NO

Question 3: can the expansion be truncated and used as a variational expression? Well YES; scheme is called MCSCF (multi-configuration self-consistent field). But still have issues: Selection of orbitals *φ*, parameters in them, … . Did we keep the variation principle? Are we capturing the physics and chemistry? Can we do the integrals?



J.C. Slater (by SBT)

Credit: So Hirata

More examples, T=0 K Variational Principle

$$\Psi_{trial}\left(1,2,\ldots,N_e\right)=\exp\left(\hat{\mathcal{T}}\right)\mathcal{A}\left[\tilde{\varphi}_a\left(1\right)\tilde{\varphi}_b\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right]$$

$$\hat{\mathcal{T}}=\sum_{j=1}^{N_e}t_{i_1\cdots i_j}^{a_1\cdots a_j}a_{a_1}^{\dagger}a_{i_1}\cdots a_{a_j}^{\dagger}a_{i_j}$$

All possible orbital substitutions in the determinant

Coupled Cluster (CC) Ansatz (single reference). *t*- amplitudes are not determined variationally in practice. Keeping all substitutions through doubles scales computationally as N_e^6

$$\Psi_{trial}\left(1,2,\ldots,N_e\right)\approx\prod_{i<j}f\left(r_{ij}\right)\mathcal{A}\left[\tilde{\varphi}_a\left(1\right)\tilde{\varphi}_b\left(2\right)\cdots\tilde{\varphi}_z\left(N_e\right)\right]$$

Jastrow correlated wave function; much used in Monte Carlo. Note: nodes are fixed by the determinant. Explicit "r12" dependence makes integrals difficult.

Why many-electron problem is tough; T=0 K Variational Principle

The variational principle

$$\mathcal{E}_0 \le \mathcal{E}_{trial} = \frac{\int \Psi^*_{trial}\,\widehat{\mathcal{H}}\,\Psi_{trial}\,d\mathbf{r}_1\ldots d\mathbf{r}_{N_e}}{\int \Psi^*_{trial}\,\Psi_{trial}\,d\mathbf{r}_1\ldots d\mathbf{r}_{N_e}}$$

is equivalent to the Schrödinger equation. That is, the Schrödinger eqn. arises from requiring the first-order variation of $\mathcal{E}_{\text{trial}}$ to be zero:

$$\delta\mathcal{E}_{trial} = \frac{\delta\mathcal{E}_{trial}}{\delta\Psi^*_{trial}}\,\delta\Psi^*_{trial} = 0$$

$$\int \delta\Psi^*_{trial}\,(\widehat{H} - \mathcal{E})\Psi_{trial}\,d\vec{r}_1\ldots d\vec{r}_{N_e} = 0$$

$$\Rightarrow \widehat{H}\Psi_0 = \mathcal{E}_0\Psi_0$$

Lagrange Multiplier to preserve normalization

So why not just guess a trial wave function with a bunch of physically and chemically plausible parameters and do the minimization calculation by brute force numerical quadrature?

Too many arbitrary forms, too many diverse parameterizations to guess, too many parameters to vary, too many variables of integration! Computational cost OK for one or a few molecules, NOT for Born-Oppenheimer Molecular Dynamics

Why many-electron problem is tough; T=0 K Variational Principle

For a normalized ground state, the energy is

$$\mathcal{E}_0 = \int \Psi_0^*\left(\mathbf{r}_1,\ldots,\mathbf{r}_{N_e}\right)\widehat{H}\Psi_0\left(\mathbf{r}_1,\ldots,\mathbf{r}_{N_e}\right)d\mathbf{r}_1\ldots d\mathbf{r}_{N_e}$$

State function: anti-symmetric under particle exchange (Fermions!)
Hamiltonian: symmetric sum of 1- and 2-body interactions.
We end up doing integrals over all but one or two of the coordinates just to eliminate them (change of variables), thus (introducing spin here):

$$\mathcal{E}_0 = \int h(\mathbf{r}_1)\gamma_{\Psi_0}\left(x_1 \mid x_1'\right)\Big|_{x_1'=x_1} dx_1 + \int g(\mathbf{r}_1,\mathbf{r}_2)\Gamma_{\Psi_0}^{(2)}\left(x_1x_2 \mid x_1'x_2'\right)\Big|_{\substack{x_1'=x_1;\\ x_2'=x_2}} dx_1dx_2$$

Sum over spins

$$\Gamma_{\Psi_0}^{(2)}\left(x_1x_2 \mid x_1'x_2'\right) := \frac{N_e\left(N_e-1\right)}{2}\int \Psi_0^*\left(\mathbf{r}_1'\sigma_1',\mathbf{r}_2'\sigma_2',\mathbf{r}_3\sigma_3,\ldots,\mathbf{r}_{N_e}\sigma_{N_e}\right)\Psi_0\left(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2,\mathbf{r}_3\sigma_3,\ldots,\mathbf{r}_{N_e}\sigma_{N_e}\right)dx_3\ldots dx_{N_e}$$

$$\gamma_{\Psi_0}\left(x_1 \mid x_1'\right) := N_e\int \Psi_0^*\left(\mathbf{r}_1'\sigma_1',\mathbf{r}_2\sigma_2,\mathbf{r}_3\sigma_3,\ldots,\mathbf{r}_{N_e}\sigma_{N_e}\right)\Psi_0\left(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2,\mathbf{r}_3\sigma_{3,}\ldots,\mathbf{r}_{N_e}\sigma_{N_e}\right)dx_2dx_3\ldots dx_{N_e}$$

2-particle reduced density matrix “2-RDM”

1-particle reduced density matrix “1-RDM”

Guessing a 2-RDM and using it in the variational principle doesn’t work either. This is the notorious *N*-representability problem: How can we know (NASC) that a trial 2-RDM comes from a N_e -Fermion wave function? The answer is known but using it is essentially as intractable as using the many-electron wave function.

Why many-electron problem is tough; T≠0 K

Grand canonical ensemble

$$\Omega(\beta|\,\tilde{\mu}) = -p(\beta|\,\tilde{\mu})V = -\beta^{-1}\ln\sum_{N_e=0}^{\infty} Tr^{(N_e)} e^{-\beta\left(\hat{\mathcal{H}}-\int d\mathbf{r}\,\tilde{\mu}(\mathbf{r})\hat{n}(\mathbf{r})\right)}$$

$$\tilde{\mu}(\mathbf{r}) := \mu - v_{ext}(\mathbf{r}) \quad ; \quad \beta = 1/(k_B T)$$

$$Tr^{(N_e)}\hat{A} := \sum_i \left\langle \Psi_i^{(N_e)} \middle| \hat{A} \middle| \Psi_i^{(N_e)} \right\rangle$$

$$\Psi_i^{(N_e)} = \text{one element of complete set } N_e \text{ fermion states}$$

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Density Functional Theory Rudiments

Hohenberg-Kohn Theorems – consider the N_e -electron Hamiltonian, which includes an external potential (for us, the nuclear-electron attraction)

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right) = -\tfrac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2 + \tfrac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|} - \sum_{i,I}^{N_e,N}\frac{Z_I}{\left|\mathbf{r}_i-\mathbf{R}_I\right|}$$

$$:= \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \equiv \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{Nuc-electr}$$

HK-I: “A given ground state density $n_0(\mathrm{r})$ determines the ground state wave function and hence all the ground state properties of an N_e -electron system.”
Original Proof: by contradiction [P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)
Modern Proof: Levy-Lieb constrained search (sequential application of the Variational Principle, density by density)
[M. Levy, Proc. Natl. Acad. Sci. USA 76, 6062 (1979); L. Lieb, Internat. J. Quantum Chem. 24, 243 (1983)]

DFT Rudiments: HK-I Proof by Contradiction

1. Consider a non-degenerate ground state. Suppose that there are two external potentials that yield the same ground-state density:

$$\hat{\mathcal{V}}_{ext}, \hat{\mathcal{V}}'_{ext} \mapsto n_0$$

2. Then by the variational principle

$$\mathcal{E}'_0 = \langle \Psi'_0 | \hat{\mathcal{H}}' | \Psi'_0 \rangle < \langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{\mathcal{H}} + \hat{\mathcal{V}}'_{ext} - \hat{\mathcal{V}}_{ext} | \Psi_0 \rangle$$

$$= \mathcal{E}_0 + \langle \Psi_0 | \hat{\mathcal{V}}'_{ext} - \hat{\mathcal{V}}_{ext} | \Psi_0 \rangle$$

$$\Rightarrow \mathcal{E}'_0 < \mathcal{E}_0 + \int d\mathbf{r}\, n(\mathbf{r}) \left[v'_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r}) \right]$$

3. But the argument can be done reversing primed and unprimed quantities. This gives

$$\mathcal{E}_0 < \mathcal{E}'_0 + \int d\mathbf{r}\, n(\mathbf{r}) \left[v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r}) \right]$$

4. Adding these last two results gives the contradiction $\mathcal{E}_0 + \mathcal{E}'_0 < \mathcal{E}_0 + \mathcal{E}'_0$

5. Therefore the ground state density determines the external potential and hence, the ground state wave function.

Remark: this proof does not address the possibility of a density *n* which is not associated with any v_{ext} (the *v*-representability problem)

DFT Rudiments: HK Theorems & Equivalence Classes (Constrained Search)

Mel Levy's idea: take all the wave-functions that give the same density and vary over them first. Then vary the density. The variational expression becomes

$$\mathcal{E}_0 \le \mathcal{E}_{trial} = \min_n \left\{ \min_{\Psi_{trial} \mapsto n} \int \Psi^*_{trial} \left(\widehat{\mathcal{H}}_{ee} + \widehat{\mathcal{V}}_{Ne} \right) \Psi_{trial} d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e} \right\}$$

$$= \min_n \left\{ \boxed{\min_{\Psi_{trial} \mapsto n} \int \Psi^*_{trial} \widehat{\mathcal{H}}_{ee} \Psi_{trial} d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e}} + \int v_{Ne}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}$$

$$\ni \quad \int \Psi^*_{trial} \Psi_{trial} d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e} = 1$$

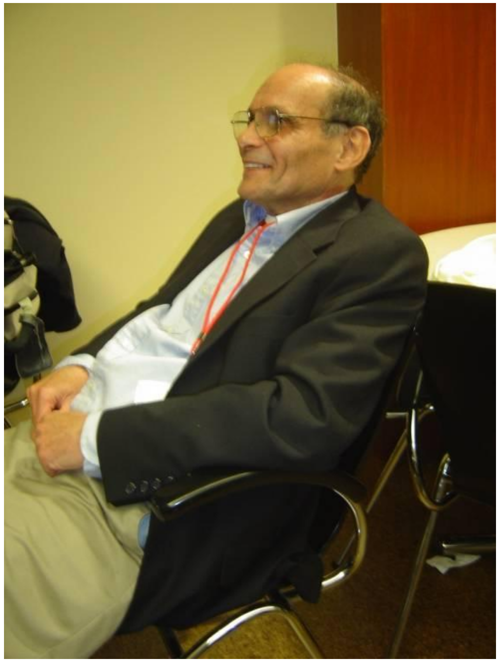
Just a rewriting but establishes the Hohenberg-Kohn theorems by *constrained search*.

HK-I: "A given ground state density $n_0(\mathbf{r})$ determines the ground state wave function and hence all the ground state properties of an N_e -electron system."

HK-II: "For such a system in an external potential $v_{ext}(\mathbf{r})$, there is a universal (*i.e.*, independent of v_{ext}) functional $F[n]$ with the following properties:

$$E_{v_{ext}}[n] = \boxed{F[n]} + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) \ge E_0$$

$$E_{v_{ext}}[n_0] = E_0 = \min_{n(\vec{r})} E_{v_{ext}}[n]$$



Mel Levy, Perdew Fest, Mar. 2008

DFT Rudiments: HK-I Proof by Constrained Search ← *blue heading means supplemental*

1. **Consider the positive operator** $\hat{\mathcal{T}}+\hat{\mathcal{V}}_{ee}$ **and form**

$$\mathcal{F}[\psi]=\langle\psi|\hat{\mathcal{T}}+\hat{\mathcal{V}}_{ee}|\psi\rangle$$

2. **Minimize this functional over all the** N_e **electron states that give** n_0

$$\mathcal{F}[\psi_0]=\min_{\psi}\langle\psi|\hat{\mathcal{T}}+\hat{\mathcal{V}}_{ee}|\psi\rangle$$

$$\ni \gamma_{\psi}(\mathbf{r}|\mathbf{r})=n_0(\mathbf{r})$$

$\gamma_{\psi}(\mathbf{r}|\mathbf{r}')$ =1-particle reduced density matrix

3. **Then at most** ψ_0 **is a normalized linear combination of ground states, since the external potential contribution to the total energy depends only on the density:**

$$\mathcal{E}_{ext}=\int d\mathbf{r}\,n_0(\mathbf{r})v_{ext}(\mathbf{r})$$

4. **Therefore the ground state density determines the ground state wave function.**

Remarks: No *v*-representability problem, no restriction to non-degenerate ground states. We have not shown that, subject to mild conditions, every density is associated with at least one N_e electron state. In fact, there are infinitely many such states for each density (Harriman, Phys. Rev. A 24, 680 (1981)).

DFT Rudiments : HK Theorems from Constrained Search (continued)

HK-II: "For an N_e –electron system with an external potential $v_{ext}(\mathbf{r})$, there exists a universal (*i.e.*, independent of v_{ext}) functional $F[n]$ with the following properties:

$$E_{v_{ext}}\left[n\right] = F\left[n\right] + \int d\mathbf{r}\, n(\mathbf{r})\, v_{ext}(\mathbf{r}) \geq E_0$$

$$E_{v_{ext}}\left[n_0\right] = E_0 = \min_{n(\vec{r})} E_{v_{ext}}\left[n\right] \quad \forall \text{ physically acceptable } n(\mathbf{r})$$

Original Proof: Essentially by announcement; the paper assumes that HK-I holds for non-ground-state densities.

Modern Proof: Levy-Lieb Constrained Search

Form

$$F\left[n\right] := \min_{\psi \mapsto n} \left\langle \psi \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \psi \right\rangle \equiv \left\langle \psi_{min;n} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \psi_{min;n} \right\rangle$$

Then

$$E_0 = \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \middle| \Psi_0 \right\rangle \leq \left\langle \psi_{min;n} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \middle| \psi_{min;n} \right\rangle$$

$$= F\left[n\right] + \int d\mathbf{r}\, n(\mathbf{r})\, v_{ext}(\mathbf{r}) := E_{v_{ext}}\left[n\right]$$

which is the first piece of the theorem.

DFT Rudiments: HK-II proof (continued)

Now apply the variational principle again

$$E_0 = \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \middle| \Psi_0 \right\rangle \le \left\langle \psi_{min;n_0} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \middle| \psi_{min;n_0} \right\rangle$$

$$\Rightarrow \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \Psi_0 \right\rangle \le \left\langle \psi_{min;n_0} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \psi_{min;n_0} \right\rangle$$

But the <u>definition of</u> $\psi_{min;n}$ means that $\left\langle \psi_{min;n_0} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \psi_{min;n_0} \right\rangle \le \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \Psi_0 \right\rangle$

Taken together, these give bracketing inequalities

$$\left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \Psi_0 \right\rangle \le \left\langle \psi_{min;n_0} \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \psi_{min;n_0} \right\rangle = F\left[n_0\right] \le \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \Psi_0 \right\rangle$$

$$\Rightarrow F\left[n_0\right] = \left\langle \Psi_0 \middle| \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} \middle| \Psi_0 \right\rangle \Rightarrow E_{v_{ext}}[n_0] = E_0$$

Remark: This *F*[*n*] , the Levy functional, is NOT the same mathematical object as the one originally defined by HK. In particular, there is no *v*-representability issue with regard to the variation over *n* nor any restriction to non-degenerate ground state. This functional <u>does</u> fulfill the role of the one defined by HK. It has its own problems however. It is not convex and has some unpleasant functional derivative problems. For most purposes, the Levy functional is good enough. See Lieb (1983).

Convexity: $A\left[an_1 + (1-a)n_2\right] \le aA[n_1] + (1-a)A[n_2]$

DFT Rudiments: Existence Thms and Proceeding Constructively (Kohn-Sham)

Recall HK-II

$$E_{v_{ext}}[n] = F[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) \geq E_0$$

$$E_{v_{ext}}[n_0] = E_0 = \min_{n(\vec{r})} E_{v_{ext}}[n] \quad \forall \text{ physically acceptable } n(\mathbf{r})$$

$$\int d\mathbf{r}\, n(\mathbf{r}) = N_e$$

Do the variation with a Lagrange multiplier for fixed particle number

$$\delta\left\{F[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) - \mu\left(\int d\mathbf{r}\, n(\mathbf{r}) - N_e\right)\right\} = 0$$

$$\Rightarrow \frac{\delta F}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}) = \mu$$

DFT Rudiments: Existence Thms and Proceeding Constructively (Kohn-Sham)

- **The big challenge: HK-II says that *F*[*n*] exists but does not give a form that can be used to do the variational problem just displayed.**
- **But we do know how to form *F*[*n*] explicitly for a system of non-interacting fermions with the same density set by some v_{KS} as follows:**

$$F[n] := \min_{\Phi\mapsto n}\left\langle\Phi\middle|\hat{\mathcal{T}}+\hat{\mathcal{V}}_{ee}\middle|\Phi\right\rangle \equiv \left\langle\Phi_{min;n}\middle|\hat{\mathcal{T}}+\hat{\mathcal{V}}_{ee}\middle|\Phi_{min;n}\right\rangle$$

$$E_{v_{KS}}[n] = F_{\text{non-inter}}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, v_{KS}(\mathbf{r})$$

$$\hat{\mathcal{V}}_{ee} = 0 \Rightarrow F_{\text{non-inter}}[n] := \mathcal{T}_S[n] = \min_{\Phi\mapsto n}\left\langle\Phi\middle|\hat{\mathcal{T}}\middle|\Phi\right\rangle \equiv \left\langle\Phi_{min;n}\middle|\hat{\mathcal{T}}\middle|\Phi_{min;n}\right\rangle$$

Non-interacting fermions means $\Phi_{min;n}$ is a Slater determinant.

$$\Phi_{min;n}(1,\ldots,N_e) = \frac{1}{\sqrt{N_e!}}\det\left|\varphi_1\ldots\varphi_{N_e}\right|$$

The Slater determinant 1- and 2-RDMs are

$$\gamma_{SD}(x\,|\,x') = \sum_{j=1}^{N_e}\varphi_j^*(x')\varphi(x)$$

$$\Gamma_{SD}^{(2)}(x_1x_2\,|\,x_1'x_2') = \frac{1}{2}\det\begin{pmatrix}\gamma_{SD}(x_1\,|\,x_1') & \gamma_{SD}(x_1\,|\,x_2') \\ \gamma_{SD}(x_2\,|\,x_1') & \gamma_{SD}(x_2\,|\,x_2')\end{pmatrix}$$

So the KS kinetic energy is

$$\mathcal{T}_s[n] \equiv \mathcal{T}_s\left[\{\varphi[n]\}\right] = -\frac{1}{2}\sum_{j=1}^{N_e}\int d\mathbf{r}\,\varphi_j^*(x)\nabla^2\varphi_j(x)$$

How is this useful?

DFT Rudiments: Existence Theorems and Proceeding Constructively (cont'd.)

By definition, the non-interacting (independent particle) system must have energy

$$E_s[n] \equiv \mathcal{T}_S\left[\left\{\varphi[n]\right\}\right] + \int d\mathbf{r}\, n(\mathbf{r}) v_{KS}(\mathbf{r})$$

Again, do the variation with a Lagrange multiplier for fixed particle number

$$\delta\left\{\mathcal{T}_S[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{KS}(\mathbf{r}) - \mu\left(\int d\mathbf{r}\, n(\mathbf{r}) - N_e\right)\right\} = 0$$

$$\Rightarrow \frac{\delta \mathcal{T}_S}{\delta n(\mathbf{r})} + v_{KS}(\mathbf{r}) = \mu$$

Choose the Lagrange multiplier to be the same as in the original system by setting the zero of the potential v_{KS} (adding a constant, if necessary).

So we may be able to map the problem into that of constructing v_{KS}.
How can that be done?

Remark: v-representability of the ground-state density n_0 has been reintroduced as an assumption.

DFT Rudiments: Kohn-Sham Rearrangement

The non-interacting system becomes useful as follows. Rearrange the interacting system functional as follows:

$$E_{v_{ext}}[n] = \mathcal{T}[n] + E_{coul}[n] + E_{ext}[n]$$

$$= \mathcal{T}_S[n] + E_{ee}[n] + \left\{ E_x[n] + E_{correl}^{quant.chem.}[n] + \mathcal{T}[n] - \mathcal{T}_S[n] \right\} + E_{ext}[n]$$

$$\equiv \mathcal{T}_S[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

$$\mathcal{T}_S[n] \equiv \tfrac{1}{2} \sum_j n_j \int d\mathbf{r} \left| \nabla \varphi_j(\mathbf{r}) \right|^2$$

$$E_{ee}[n] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$n(\mathbf{r}) \equiv \sum_{j=1}^{N_F} n_j \left| \varphi_j(\mathbf{r}) \right|^2 ;$$

$$0 \le n_j \le 1, 2 \text{ (depending on spins)}$$

Lu Jeu Sham, Sanibel, 2010.

DFT Rudiments: Details of the Kohn-Sham Construction -

What we have done is

$$E_{v_{ext}}[n] := F[n] + E_{ext}[n] = \mathcal{T}_S[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

$$F[n] = \mathcal{T}_S[n] + E_{ee}[n] + E_{xc}[n]$$

Thus, the variation principle and Euler equation for the physical system become

$$\delta\left\{F[n] + \int d\mathbf{r}\, n(\mathbf{r}) v_{ext}(\mathbf{r}) - \mu\left(\int d\mathbf{r}\, n(\mathbf{r}) - N_e\right)\right\} = 0$$

$$\Rightarrow \frac{\delta \mathcal{T}_S}{\delta n(\mathbf{r})} + v_{ee}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}) = \mu$$

Comparison with the Euler Equation for the KS system $\frac{\delta \mathcal{T}_S}{\delta n(\mathbf{r})} + v_{KS}(\mathbf{r}) = \mu$

shows that $v_{KS}(\mathbf{r}) = v_{ee}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r})$

New task: construct E_{xc}

Rudiments of K-S DFT

The Kohn-Sham equation (non-spin-polarized for simplicity) is:

$$\left\{-\tfrac{1}{2}\nabla^2-\sum_I\frac{Z_I}{\left|\mathbf{r}_1-\mathbf{R}_I\right|}+\int d\mathbf{r}_2\,\frac{n_{\{\vec{R}\}}(\mathbf{r}_2)}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}+v_{xc}(\mathbf{r}_1)\right\}\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)=\varepsilon_j^{KS}\,\phi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)$$

with the eXchange-Correlation potential given by $v_{xc}[n]=\dfrac{\delta E_{xc}}{\delta n}$

Everything is known except for the XC functional E_{XC}. It is known exactly only in a few special cases.

Remark: $\mathcal{T}_S[n]:=\min\limits_{\Phi\mapsto n}\langle\Phi|\hat{\mathcal{T}}|\Phi\rangle$

$$\equiv\tfrac{1}{2}\sum_j n_j\int d\mathbf{r}\left|\nabla\varphi_j(\mathbf{r})\right|^2$$

Φ = the Kohn-Sham determinant

Remark: Exact exchange in DFT is defined by the KS determinant, NOT the Hartree-Fock determinant.

Rudiments of K-S DFT

$$v_{xc}\left[n\right] = \frac{\delta E_{xc}}{\delta n}$$

There are several classes of approximate functionals that are demonstrably successful at different levels of prediction:

◊ Local Density Approximation

$$E_{xc}\left[n\right] = \int d\vec{r}\; n_{\{\vec{R}\}}(\mathbf{r}) U_{xcLDA}[n_{\{\mathbf{R}\}}(\mathbf{r})] =$$

$$\int d\mathbf{r}\; n_{\{\mathbf{R}\}}(\mathbf{r}) \left\{ n^{1/3}_{\{\mathbf{R}\}}(\mathbf{r}) F_{LDA}[n_{\{\mathbf{R}\}}(\mathbf{r})] \right\}$$

F_{LDA} = constant → original LDA, also $X\alpha$

F_{LDA} = dimensionless functional of density only → later LDAs (Hedin-Lundqvist, Perdew-Zunger, Vosko-Wilk-Nussair)

◊ Generalized Gradient approximations add terms dependent on density gradients:

$$E^{GGA}_{xc}\left[n\right] = \int d\mathbf{r}\; n_{\{\mathbf{R}\}}(\mathbf{r}) U_{xcGGA}[n_{\{\mathbf{R}\}}(\mathbf{r}), s(\mathbf{r})]$$

$$= \int d\mathbf{r}\; n_{\{\mathbf{R}\}}(\mathbf{r}) \left\{ n^{1/3}_{\{\mathbf{R}\}}(\mathbf{r}) F_{GGA}[n_{\{\mathbf{R}\}}(\mathbf{r}), s(\mathbf{r})] \right\}$$

$$s(\mathbf{r}) = \left|\nabla n\right| \Big/ \left\{ 2(3\pi^2)^{1/3} n^{4/3} \right\}$$

a) F_{GGA} determined by constraints, scaling inequalities, other exact results: Perdew-Wang 91, Perdew-Burke- Ernzerhof, VMT, VT{84} PBEmol, (Mexican DFT collaboration), etc.

b) F_{GGA} determined in part by fitting to atomization energies: Becke etc.

Free Energy Density Functional Theory

Mermin-Hohenberg-Kohn finite-temperature DFT
Basic equations are:

$$\mathcal{F}_{v_{ion}}\left[n\right] = \mathcal{T}\left[n\right] + E_{coul}\left[n\right] + E_{ion}\left[n\right] - T\mathcal{S}[n]$$

$$= \mathcal{T}_S\left[n\right] - T\mathcal{S}_s[n] + E_{ee}\left[n\right] + E_{ion}\left[n\right]$$

$$+\left\{E_x\left[n\right] + E_{correl}^{quant.chem.}\left[n\right] + \mathcal{T}\left[n\right] - \mathcal{T}_S\left[n\right] - T\left(\mathcal{S}[n] - \mathcal{S}_s[n]\right)\right\}$$

$$:= \mathcal{T}_S\left[n\right] - T\mathcal{S}_s[n] + E_{ee}\left[n\right] + \mathcal{F}_{xc}\left[n\right] + E_{ion}\left[n\right]$$

$$\mathcal{T}_S\left[n\right] := \tfrac{1}{2}\sum_j \left(1 + \exp\left\{\beta\left(\varepsilon_j - \mu\right)\right\}\right)^{-1} \int d\mathbf{r}\left|\nabla\varphi_j\left(\mathbf{r}\right)\right|^2 \equiv \tfrac{1}{2}\sum_j f_j \int d\mathbf{r}\left|\nabla\varphi_j\left(\mathbf{r}\right)\right|^2$$

$$E_{ee}\left[n\right] = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}; \qquad E_{ion}\left[n\right] = \int d\mathbf{r}\, n(\mathbf{r}) v_{ion}(\mathbf{r})$$

$$n\left(\mathbf{r}\right) := \sum_j \left(1 + \exp\left\{\beta\left(\varepsilon_j - \mu\right)\right\}\right)^{-1} \left|\varphi_j\left(\mathbf{r}\right)\right|^2 \equiv \sum_j f_j \left|\varphi_j\left(\mathbf{r}\right)\right|^2$$

$$\beta = 1/k_B T$$

$E_{ion\text{-}ion}$ omitted for brevity.

K-S Free-energy DFT

$$v_{xc}[n] = \frac{\delta \mathcal{F}_{xc}}{\delta n}$$

$$n(\mathbf{r}) := \sum_j \left(1 + \exp\left\{\beta\left(\varepsilon_j - \mu\right)\right\}\right)^{-1} \left|\varphi_j(\mathbf{r})\right|^2 \equiv \sum_j f_j \left|\varphi_j(\mathbf{r})\right|^2$$

Otherwise the KS equations look the same as in the ground state.

Thermal Hartree-Fock Approximation

Mermin [Ann. Phys. (NY) 21, 99 (1963)] proved that the Finite Temperature Hartree-Fock approximation is the “obvious” generalization of ground-state Hartree-Fock theory. Basic equations are:

$$\mathcal{F}_{HF}\left[\{\phi\}\right] = \Omega_{HF}(\beta\,|\,\{\phi\}) + \int d\mathbf{r}\left[\mu - v_{ion}(\mathbf{r})\right]n(\mathbf{r})$$

$$\Omega_{HF}(\beta\,|\,\{\phi\}) = -\beta^{-1}\ln\sum_{N_e=0}^{\infty}\mathrm{Tr}^{(N_e,SD)}e^{-\beta\left(\hat{H}_{ee}-\int d\mathbf{r}[\mu-v_{ion}(\mathbf{r})]n(\mathbf{r})\right)}$$

$$\mathcal{F}_{HF}\left[\{\phi\}\right] = \mathcal{T}_{HF}\left[\{\phi\}\right] - T\mathcal{S}_{HF}[\{\phi\}] + E_{ee}\left[\{\phi\}\right] + E_{ex}\left[\{\phi\}\right] + E_{ion}[n]$$

$$\mathcal{T}_{HF}\left[\{\phi\}\right] := \tfrac{1}{2}\sum_{j} f_j\int d\mathbf{r}\left|\nabla\varphi_j(\mathbf{r})\right|^2 \quad ; \quad \mathcal{S}_{HF}[\{\phi\}] := -k_B\sum_{j}\left[f_j\ln f_j + (1-f_j)\ln(1-f_j)\right]$$

$$E_{ee}\left[\{\phi\}\right] = \frac{1}{2}\sum_{ij} f_i f_j\int d\mathbf{r}_1 d\mathbf{r}_2\,\frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}$$

$$E_{ex}\left[\{\phi\}\right] = -\frac{1}{2}\sum_{ij} f_i f_j\delta_{\sigma_i\sigma_j}\int d\mathbf{r}_1 d\mathbf{r}_2\,\frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}$$

$$f_j := \left(1+\exp\left\{\beta\left(\varepsilon_j-\mu\right)\right\}\right)^{-1} \quad ; \quad \beta := 1/k_B T$$

The trace “N_e,*SD*” is over all N_e-electron Slater determinants Φ.

Thermal Hartree-Fock Approximation - continued

Variational minimization leads to the obvious generalization of the ground-state HF equation:

$$\varepsilon_i \phi_i(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 + v_{ion}(\mathbf{r}) \right) \phi_i(\mathbf{r}) + \sum_j f_j \int d\mathbf{r}_2 \frac{\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}\phi_i(\mathbf{r})$$

$$-\sum_j f_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}_2 \frac{\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}\phi_j(\mathbf{r})$$

Topics

- ❖ Motivation: Physics of Warm Dense Matter: see M. Desjarlais on 12 Mar. and F. Graziani on 13 Mar.
- ❖ Survey
    - ▪ Problems of naïve variational theory (Zero T, finite T)
    - ▪ Implications for molecular dynamics on complicated materials
    - ▪ Density functional theory basics – Zero T, finite T
    - ▪ Finite-T Hartree-Fock
    - ▪ Open questions for WDM applications
- ❖ Challenge: Orbital-free functionals
- ❖ Progress: New functionals, new reference calculations

DFT for WDM – Major Open Questions

- **Temperature and density dependence of $\mathcal{F}_{\mathrm{xc}}$?**
- **Implicit temperature dependence of ground-state $E_{xc}[n]$ used at finite T. Is $\mathcal{F}_{\mathrm{xc}}[n, T] \approx E_{xc}[n(T)]$ good enough?**
- **Same question for ground state OF-KE functionals: $\mathcal{T}_s[n,T] \approx \mathcal{T}_s[n(T)]$?**
- ***Orbital-free* free-energy functionals in WDM regime -**

$$\mathcal{T}_s[n,T] = ?$$

$$\mathcal{S}_s[n,T] = -k_B \sum_j \left\{ f_j \ln f_j + (1 - f_j) \ln(1 - f_j) \right\} = ?$$

$$\mathcal{F}_{xc}[n,T] = ?$$

Functional forms for $t_S[n, T]$, $s_S[n,T]$, $u_{xc}[n,T]$?
Accurate ground-state limiting forms?

- **Observation: OF-DFT may be necessary, not merely an attractive option for WDM. Large numbers of small occupation numbers make the number of MD steps comparatively small for conventional KS at finite T .**
- **Technical issue: pseudopotentials? (mean ionization state?)**

Topics

- ❖ **Motivation: Physics of Warm Dense Matter: see M. Desjarlais on 12 Mar. and F. Graziani on 13 Mar.**
- ❖ **Survey**
    - **Problems of naïve variational theory (Zero T, finite T)**
    - **Implications for molecular dynamics on complicated materials**
    - **Density functional theory basics – Zero T, finite T**
    - **Finite-T Hartree-Fock**
    - **Open questions for WDM applications**
- ❖ **Challenge: Orbital-free functionals**
- ❖ **Progress: New functionals, new reference calculations**

B-O Forces from DFT

- The KS eigenvalue problem is the high-cost computational step in B-O MD. At *every* step:

$$n_{\{\mathbf{R}\}}(\mathbf{r}) = \sum_k f_k(T)\,|\phi_{k\{\mathbf{R}\}}(\mathbf{r})|^2 \ \text{for each configuration} \ \{\mathbf{R}\}$$

$$\hat{h}^{KS}_{\{\mathbf{R}\}}\varphi_{k;\{\mathbf{R}\}}(\mathbf{r}) = \varepsilon_{k;\{\mathbf{R}\}}\varphi_{k;\{\mathbf{R}\}}(\mathbf{r})$$

$$\hat{h}^{KS}_{\{\mathbf{R}\}} = -\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r};\{\mathbf{R}\})$$

$$v_{KS}(\mathbf{r};\{\mathbf{R}\}) = v_{ion}(\mathbf{r};\{\mathbf{R}\}) + v_{H;\{\mathbf{R}\}}(\mathbf{r}) + v_{xc;\{\mathbf{R}\}}(\mathbf{r})$$

Too slow! Order N_e^M with $2.6 \le M \le 3$ at best. Requires heroic calculations (some of which have been done – need for the data is HIGH!)

There are "order-*N*" approximate methods but they are not general (additional assumptions, e.g. about basis locality, etc., limit applicability).

→ So there's both urgency and opportunity for better methods. Or do we just wait on bigger, faster machines?

“Everyone knows Amdahl’s Law but quickly forgets it”

T.Puzak, IBM (2007)

$$S = \frac{1}{(1-P)+\dfrac{P}{N}}$$

99.9 % parallel, 2048 processors , speedup ≈ 675

S = speedup; P = fraction parallel; N = number of processors

Amdahl’s Law in the Multicore Era

Mark D. Hill, University of Wisconsin-Madison
Michael R. Marty, Google

Augmenting Amdahl’s law with a corollary for multicore hardware makes it relevant to future generations of chips with multiple processor cores. Obtaining optimal multicore performance will require further research in both extracting more parallelism and making sequential cores faster.

IEE Computer, <u>41</u>, 33 (2008)

Also see *www.cs.wisc.edu/multifacet/papers/amdahl_multicore.ppt*

The Ideal - Orbital-free DFT

With the K-S density kernels t_s, s_S and a good density-dependent (NOT orbital-dependent) $\mathcal{F}_{XC}$, DFT B-O forces would be simple:

$$\mathcal{T}_s[n,T] = \int d\mathbf{r}\; t_S[n(\mathbf{r}),T] = \tfrac{1}{2}\sum_k f_k(T)\int d\mathbf{r}\left|\nabla\varphi_k(\mathbf{r})\right|^2$$

$$\mathcal{S}_s[n,T] = -k_B\int d\mathbf{r}\; s_S[n(\mathbf{r}),T] = -k_B\sum_k\left\{ f_k \ln f_k + (1-f_k)\ln(1-f_k)\right\}$$

$$\frac{\delta(\mathcal{T}_s)}{\delta n} + v_{KS}[n(\mathbf{r})] = \mu$$

Even at *T*=0, there are many well-known barriers to getting t_s , *e.g.*, Teller non-binding theorem for Thomas-Fermi-Dirac, failures of TF-von Weizsäcker, ….

L.H. Thomas, Sanibel, 1975.

Photo by SBT

Scaled Thomas-Fermi-von Weiszäcker

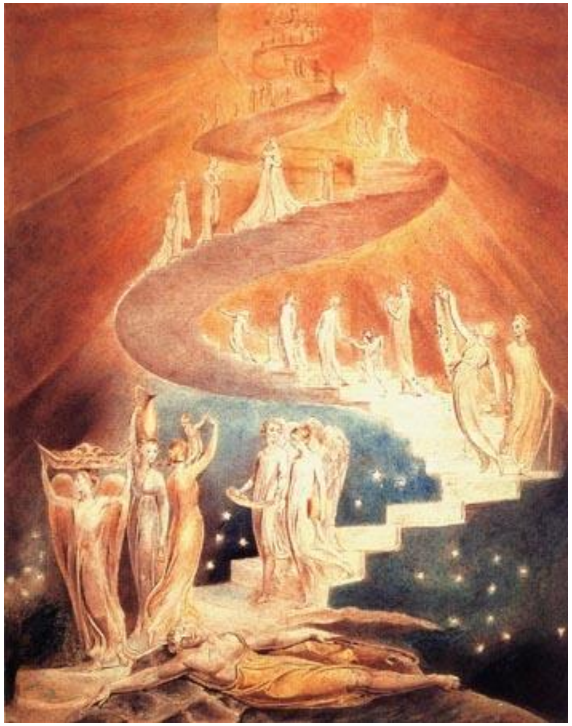
$$\mathcal{T}_{TF\lambda W}[n] := \mathcal{T}_{TF} + \lambda_W \mathcal{T}_W \quad , \qquad 0 \le \lambda_W \le 1$$

$$\mathcal{T}_{TF}[n] := c_{TF}\int d\mathbf{r}\; n^{5/3}(\mathbf{r}) \quad , \quad c_{TF} == \frac{3}{10}(3\pi^2)^{2/3}$$

$$\mathcal{T}_W[n] := \frac{1}{8}\int d\mathbf{r}\,\frac{\left|\nabla n(\mathbf{r})\right|^2}{n(\mathbf{r})}$$

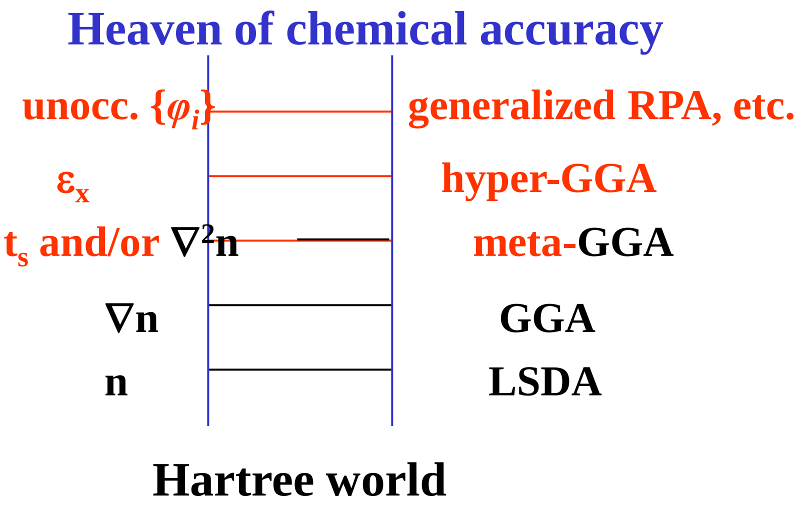
The Other KS Orbital Problem (Jacob's Ladder)

Biblical (Genesis 28: 11-19)



William Blake, 1800; Also African-American Spiritual (folk hymn)

- **DFT – XC approximations (John Perdew)**



Heaven of chemical accuracy

unocc. $\{\varphi_i\}$ — **generalized RPA, etc.**

ε_x — **hyper-GGA**

t_s and/or $\nabla^2 n$ — **meta-GGA**

∇n — **GGA**

n — **LSDA**

Hartree world

Red = explicit orbital dependence

J. P. Perdew and K. Schmidt, in *Density Functional Theory and its Application to Materials*, V. Van Doren, C. Van Alsenoy, and P. Geerlings, Eds., AIP, Melville, New York, 2001

Dilemma: "Everybody" is working on orbital-dependent XC functionals!
See Mexican Group work on "lower rung" XC functionals

Orbital-free KE Approaches – Response Function

Here, in somewhat sloppy translationally invariant notation, is the basic theme of the response function approach

$$\delta n(\mathrm{r}) = \int d\mathrm{r}'\, \chi(\mathrm{r} - \mathrm{r}')\, \delta v_{KS}(\mathrm{r}') \Rightarrow \delta n(\mathrm{q}) = \chi(\mathrm{q})\, \delta v_{KS}(\mathrm{q})$$

$$\delta(\mathrm{r} - \mathrm{r}') = \int d\mathrm{r}''\, \frac{\delta n(\mathrm{r})}{\delta v_{KS}(\mathrm{r}'')}\, \frac{\delta v_{KS}(\mathrm{r}'')}{\delta n(\mathrm{r}')} \Rightarrow \delta(\mathrm{q} - \mathrm{q}') = \chi(\mathrm{q})\, \frac{\delta v_{KS}}{\delta n}(\mathrm{q},\mathrm{q}')$$

$$\frac{\delta \mathcal{T}_s}{\delta n} + v^{KS}[n(\mathrm{r})] = \mu \quad \Rightarrow \quad \delta(\mathrm{q} - \mathrm{q}') = -\chi(\mathrm{q})\, \frac{\delta^2 \mathcal{T}_s}{\delta n\, \delta n}(\mathrm{q},\mathrm{q}')$$

Result is a set of non-local (two-point) approximations based on Average Density Approximation, Weighted Density approximation, etc.
Various versions work moderately well for metals.
Another recent version works moderately well for insulators.
The non-locality is too complicated (computationally costly, introduces local pseudo-potentials) for our purposes

Orbital-free KE Approaches – Response Function

Density-dependent kernel for semiconductors

C. Huang and E.A. Carter, Phys. Rev. B 81, 045206 (2010)

$$\mathcal{T}_s[n] = \mathcal{T}_{TF} + \mathcal{T}_W + \mathcal{T}_\theta^{\alpha,\beta}$$

$$\mathcal{T}_\theta^{\alpha,\beta} = c_0 \int d\mathrm{r}d\mathrm{r}' \, n^\alpha(\mathrm{r})\, n^\beta(\mathrm{r}')\, w_{\alpha\beta}[\mathrm{r},\mathrm{r}']$$

$$w_{\alpha\beta}(\mathrm{r},\mathrm{r}') := w\left[k_F(\mathrm{r})(1+\lambda x^2)\left|\mathrm{r}\text{-}\mathrm{r}'\right|\right]$$

$$k_F = (3\pi^2 n)^{1/3} \qquad x = \frac{|\nabla n|}{n^{4/3}}$$

$$\alpha = \frac{8}{3} - \beta \qquad \beta \approx 0.65 \to 0.89$$

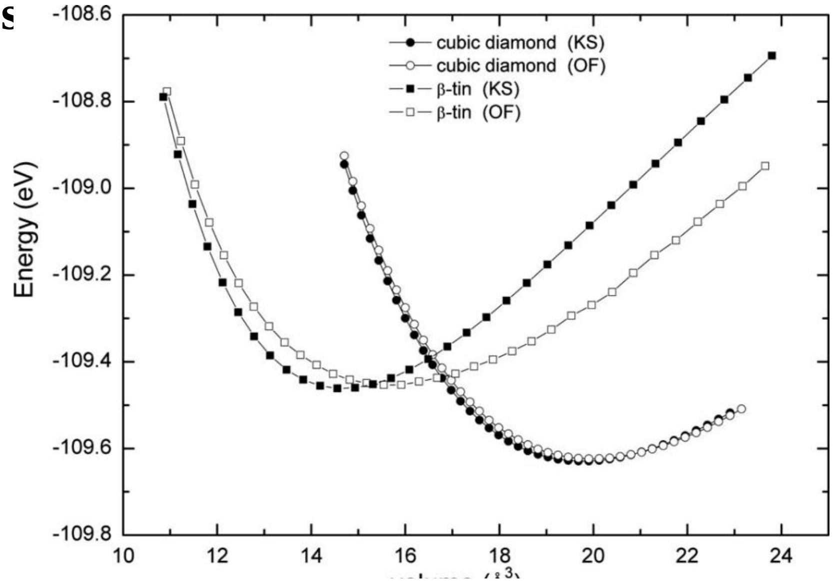


FIG. 1. OF-DFT and KS-DFT total energy versus volume curves for CD and β-tin silicon. For CD silicon, the optimal KEDF parameters are used (λ=0.01 and β=0.65). For β-tin silicon, the optimal λ=0.0055 is used with β=0.65 (optimal for CD silicon).

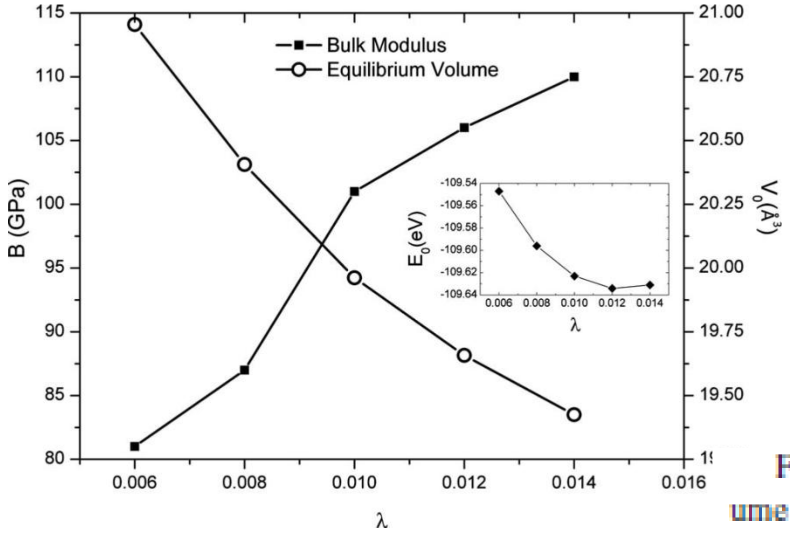


FIG. 3. Variation in CD silicon bulk modulus, equilibrium volume per atom, and total energy per atom with different λ.

Two-point OFKE Functional Problems

- ❖ **Density-independent kernels suffer from nonlinear instability " … in the sense that the corresponding kinetic-energy functionals are not bounded from below."** X. Blanc and E. Cancès, J. Chem. Phys. 122, 214106 (2005) ***N*-representability issue?**

- ❖ **Introducing density-dependence in the kernel "… comes at the expense of greatly complicating the derivation and making a straightforward numerical implementation computationally expensive…"** Y.A. Wang, N.Govind, and E.A.Carter, Phys. Rev. B 60, 16350 (1999)

- ❖ **Different kernels for metals and semi-conductors: but what about pressure-induced insulator-metal transitions?**

- ❖ **Reference density is non-unique for bulk systems and undefined for finite ones.**

- ❖ **Multiple parameters without physical constraints.**

Orbital-free Density Functional Theory: Single-Point Strategy

- **Goal: a workable recipe for a one-point $t_s[n]$ purely for driving MD. Remember the ground state formulation:**

$$E[n] = \mathcal{T}_s[n] + E_{ee}[n] + E_{xc}[n] + E_{ne}[n]$$

$$\mathcal{T}_s[n] = \int d\mathrm{r}\; t_S[n(\mathrm{r})] = -\frac{1}{2}\sum n_i \int d\mathrm{r}\; \varphi_i^*(\mathrm{r})\nabla^2\varphi_\mathrm{i}(\mathrm{r})$$

$$\vec{F}_{I,electronic} = -\nabla_I\, E[n] = -\int dr \left[\frac{\delta\mathcal{T}_s}{\delta n} + v_{KS}[n(\mathrm{r})]\right]\nabla_I\, n(\mathrm{r}) - \int d\mathrm{r}\, n(\mathrm{r})\nabla_I v_{ne}$$

- **Observe: we do NOT seek a KE density kernel that will do everything that is in the basic DFT theorems**

- **Desired: $t_s[n(r)]$ be no more complicated than GGA E_{XC} (depends on gradient of the density) or meta-GGA (depends on Laplacian of the density also).**

- **Assumption: continued progress on *pure* E_{XC} approximations, i.e., *not* hybrids or OEP (optimized effective potential).**

- **Obviously need analogous progress for $T > 0$ K: $t_S\,[n, T]$, $s_S\,[n,T]$, $u_{xc}\,[n,T]$**

Single-point OF-KE Functional Construction

- **Key Ingredient - Pauli KE, Pauli potential, and square root of density** **[M. Levy and H. Ou-Yang, Phys. Rev. B 38, 625 (1988); A. Holas and N.H. March, Phys. Rev. A 44, 5521 (1991); E.V. Ludeña, V.V. Karasiev, R. López-Boada, E. Valderama, and J. Maldonado, J. Comp. Chem. 20, 155 (1999) and references in these]** **An exact expression is**

$$\mathcal{T}_s[n] = \mathcal{T}_W[n] + \mathcal{T}_\theta[n], \quad \mathcal{T}_\theta[n] \ge 0$$

Stationarity of variation with respect to density *n* yields

$$\left(-\frac{1}{2}\nabla^2 + v_{KS}(\mathrm{r}) + v_\theta(\mathrm{r})\right)\sqrt{n(\mathrm{r})} = \mu\sqrt{n(\mathrm{r})}$$

$$v_\theta(\mathrm{r}) = \delta T_\theta / \delta n \;\ge 0 \quad \forall\, \mathrm{r}$$

- **Useful (but incorrect) clue: “Conjointness conjecture”** **[H. Lee, C. Lee, and R.G. Parr, Phys. Rev. A 44, 768 (1991)].** **The GGA E_X is**

$$E_x^{GGA}[n] = -c_x \int d\mathrm{r}\; n^{4/3}(\mathrm{r}) F_x\left(s(\mathrm{r})\right)$$

$$s(\mathrm{r}) = |\nabla n| \big/ \left\{2(3\pi^2)^{1/3} n^{4/3}\right\}$$

- **Conjointness:**

$$\mathcal{T}_s^{GGA}[n] = \int d\mathrm{r}\; n^{5/3}(\mathrm{r}) F_t\left(s(\mathrm{r})\right)$$

$$F_t\left(s(\mathrm{r})\right) \propto F_x\left(s(\mathrm{r})\right)$$

OF-DFT: Test of Existing Single-point (GGA) KE functionals

- **Tests of 6 existing functionals, three conjoint. KS density as input to each.**

PW91: Lacks and Gordon, J.Chem. Phys. 100, 4446 (1994) **[conjoint]**

PBE-TW: Tran and Wesolowski, Internat. J. Quantum Chem. 89, 441 (2002) **[conjoint]**

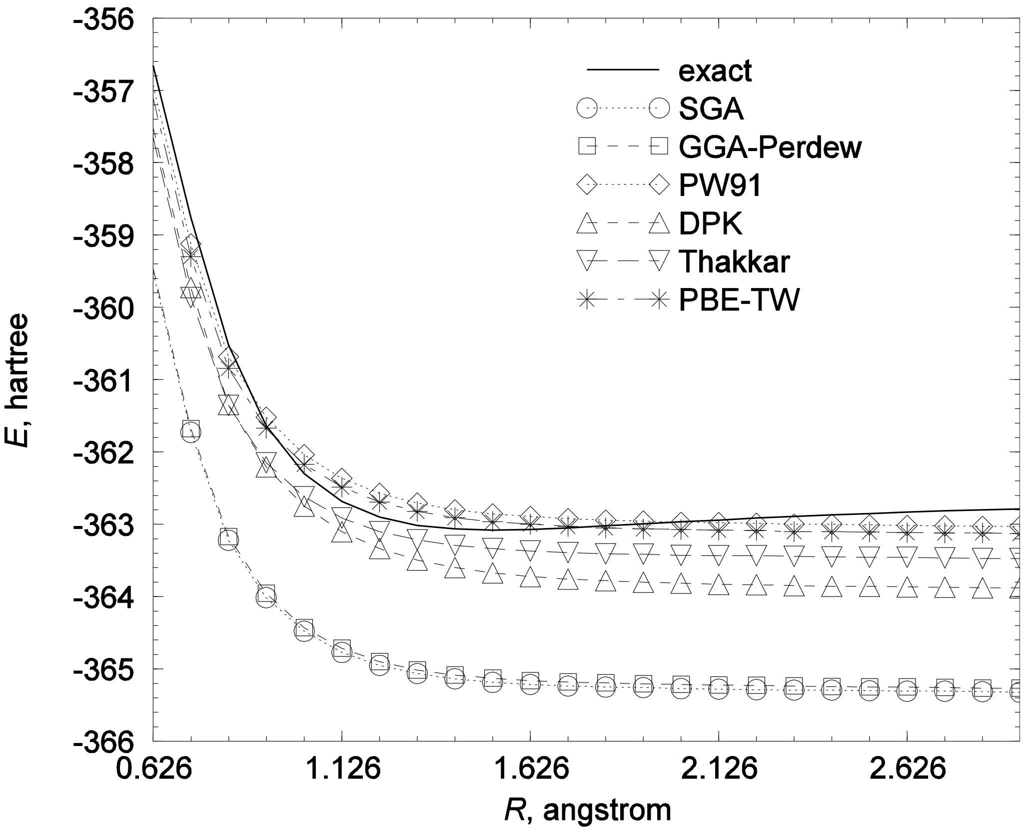
GGA-Perdew: Perdew, Phys. Lett. A 165, 79 (1992) **[conjoint]**

DPK: DePristo and Kress, Phys. Rev. A 35, 438 (1987)

Thakkar: Thakkar, Phys. Rev. A 46, 6920 (1992)

SGA: Second order Gradient Approx.

$\mathcal{T}_S = \mathcal{T}_{TF} + (1/9)\,\mathcal{T}_W$



All six $\mathcal{T}_s$ approximations fail to bind! V_θ violates positivity.

SiO Stretch; Total energy vs. bond length

J. Comput. Aided Matl. Design 13, 111 (2006)

OF-DFT: Modified conjoint KE functionals

Parameterizations

• Tried two simple forms for modified enhancement factors. These forms would be convenient for use in MD. No guarantee that any of these is optimal.

$$F_t^{PBE-N}(s) = 1 + \sum_{j=1}^{N-1} c_j \left(\frac{s^2}{1+a\,s^2} \right)^j$$

N=2 **is typical PBE form as also used by Tran & Weslowski**
N=3 **is the form used by Adamo and Barone** [J. Chem. Phys. **116**, 5933 (2002)]
N=4 **highest tried**

$$F_t^{\exp 4} = C_1(1-e^{-a_1 s^2}) + C_2(1-e^{-a_2 s^2})$$

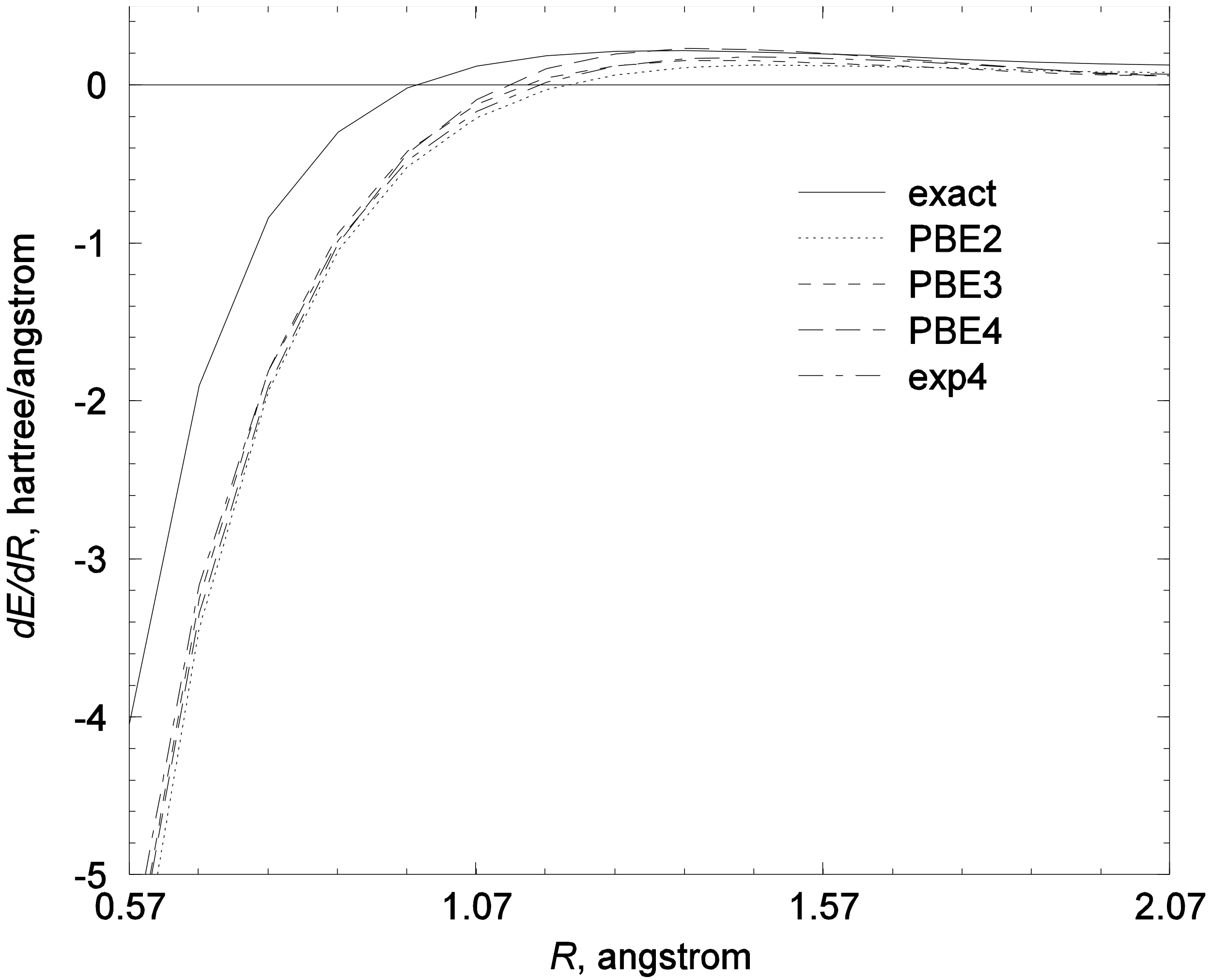
- **Constrain parameters to** $v_\theta \geq 0$

Initial parameterization used
(a) single SiO or
(b) SiO, H_4SiO_4, and $H_6Si_2O_7$.
Stretched single Si-O bond in all cases with self-consistent KS densities.

OF-DFT - Performance of Modified Conjoint, Positive-definite Functionals

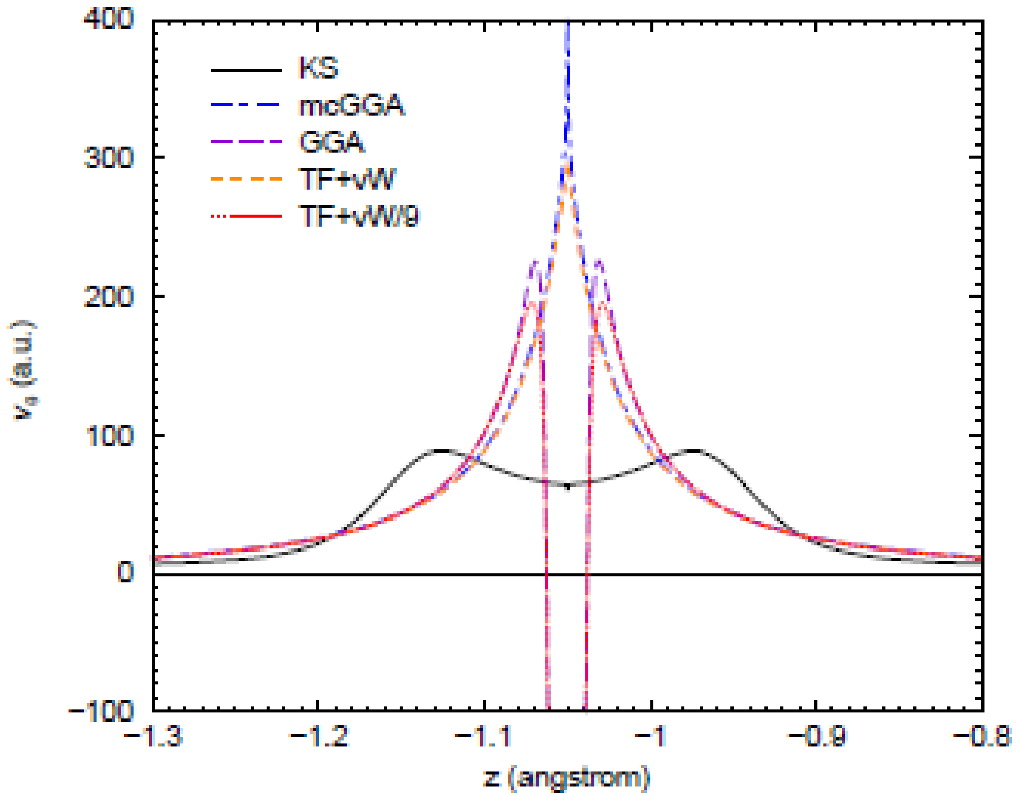
Single bond stretching gradient in H_2O.

OF-KE parameters from 3-member training set (SiO, H_4SiO_4, and $H_6Si_2O_7$) except PBE2.
NO information about H_2O in the set.



All of our functionals give too large an equilibrium bond length.

OF-DFT - Pauli Potentials Compared



Pauli potential v_θ , vicinity of the Si site in SiO at R = 1.926 Å.

"KS" is the exact inversion from the KS solution.

"GGA" is the Tran -Wesolowski potential.

"mcGGA" is our PBE2 modified conjoint-form (positivity enforced).

TF+vW and scaled TF+vW/9 for comparison.

PROBLEM:

mcGGA Pauli potential v_θ singularities at the nuclei. TOO positive! GGA goes negative. TF+vW/9 does too but TF+vW doesn't ⇒ any answer you want with TF+λvW!

Phys. Rev. B 80, 245120 (2009)
Comput. Phys. Commun. (submitted)

Orbital-free KE – Problems with Simple Approaches

Beware of scaled Thomas-Fermi-von Weiszäcker used variationally in OF-DFT, or even with the actual KS n_0 (for a given XC) as input, can lead to weirdness:

Functional **(all simple LDA XC)**	**E_{total} (Hartree)**
TFλW, $\lambda_W = 1$	**-85.734**
TFλW, $\lambda_W = 1/5$	**-128.801**
TFλW, $\lambda_W = 1/9$	**-139.887**
KS (13s8p GTO)	**-127.484**

TFλW from G. Chan, A. Cohen, and N. Handy, J. Chem. Phys. **114**, 631 (2001)

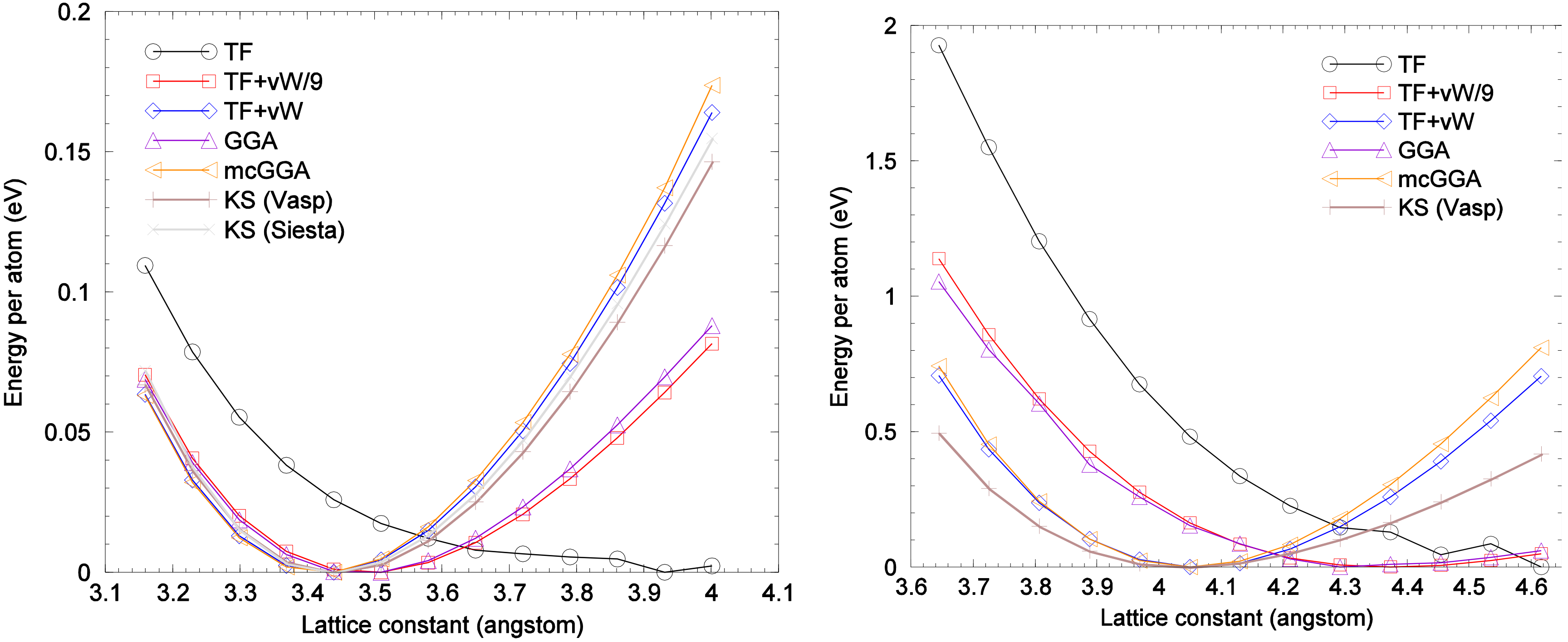
$$\mathcal{T}_{TF\lambda W}[n] := \mathcal{T}_{TF} + \lambda_W \mathcal{T}_W$$

$$E_{TFW}[n] = \mathcal{T}_{TF\lambda W}[n] + E_{ee}[n] + E_{xc}[n] + E_{ne}[n]$$

$$E_{TF\lambda W}[n_{0,TF\lambda W}] < E_{KS}[n_{0,KS}]$$

Paul Ayers (Sanibel 2007): "An *ab initio* quantum chemist will wonder- "Is an *N*-representability constraint missing?"
"If so, should we surrender? *N*-representability problems are very difficult …."

Are Positive Singularities Fatal to mcGGA?



Singularities are not fatal.

Left: Bcc Li lattice constant; Right fcc Al lattice constant. mcGGA is our PBE-2, parameterized to SiO implemented in modified PROFESS code. GGA=Tran-Wesołowski

Comput. Phys. Commun. (submitted)

Solving the OFKE Euler equation with a KS code?

Why did we switch to the PROFESS code?

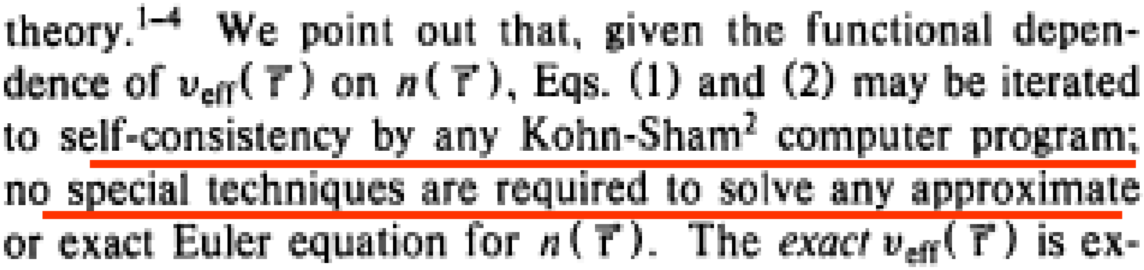
$$\mathcal{T}_s[n] = \mathcal{T}_W[n] + \mathcal{T}_\theta[n], \quad \mathcal{T}_\theta[n] \geq 0$$

Stationarity of variation with respect to density *n* yields

$$\left(-\frac{1}{2}\nabla^2 + v_{KS}(\mathrm{r}) + v_\theta(\mathrm{r})\right)\sqrt{n(\mathrm{r})} = \mu\sqrt{n(\mathrm{r})}$$

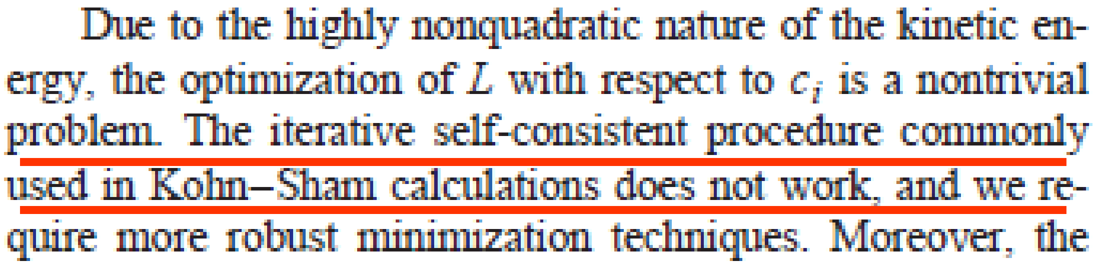
$$v_\theta(\mathrm{r}) = \delta\mathcal{T}_\theta / \delta n \ \geq 0 \quad \forall\, \mathrm{r}$$

Levy, Perdew, and Sahni, Phys. Rev. A 30, 2745 (1984)



theory.[1–4] We point out that, given the functional dependence of $v_{\mathrm{eff}}(\vec{r})$ on $n(\vec{r})$, Eqs. (1) and (2) may be iterated to self-consistency by any Kohn-Sham[2] computer program; no special techniques are required to solve any approximate or exact Euler equation for $n(\vec{r})$. The *exact* $v_{\mathrm{eff}}(\vec{r})$ is ex-

Chan, Cohen, and Handy J. Chem. Phys. 114, 631 (2001)



Due to the highly nonquadratic nature of the kinetic energy, the optimization of L with respect to c_i is a nontrivial problem. The iterative self-consistent procedure commonly used in Kohn–Sham calculations does not work, and we require more robust minimization techniques. Moreover, the

Solving the OFKE Euler equation with a KS code?

TFDvW, $\lambda_W = 1$ E_{total} (Hartree)	Chan, Cohen & Handy	Numerical KS code	GTO KS code
H atom	-0.2618	-0.26183	-0.25997
Li atom	-4.1054	-4.10542	-4.09635
Ne atom	-85.7343	-85.73445	-85.73004

However, with simple linear mixing of densities and starting from the pure von Weizsäcker KE, the iterative convergence is very slow and unpredictable

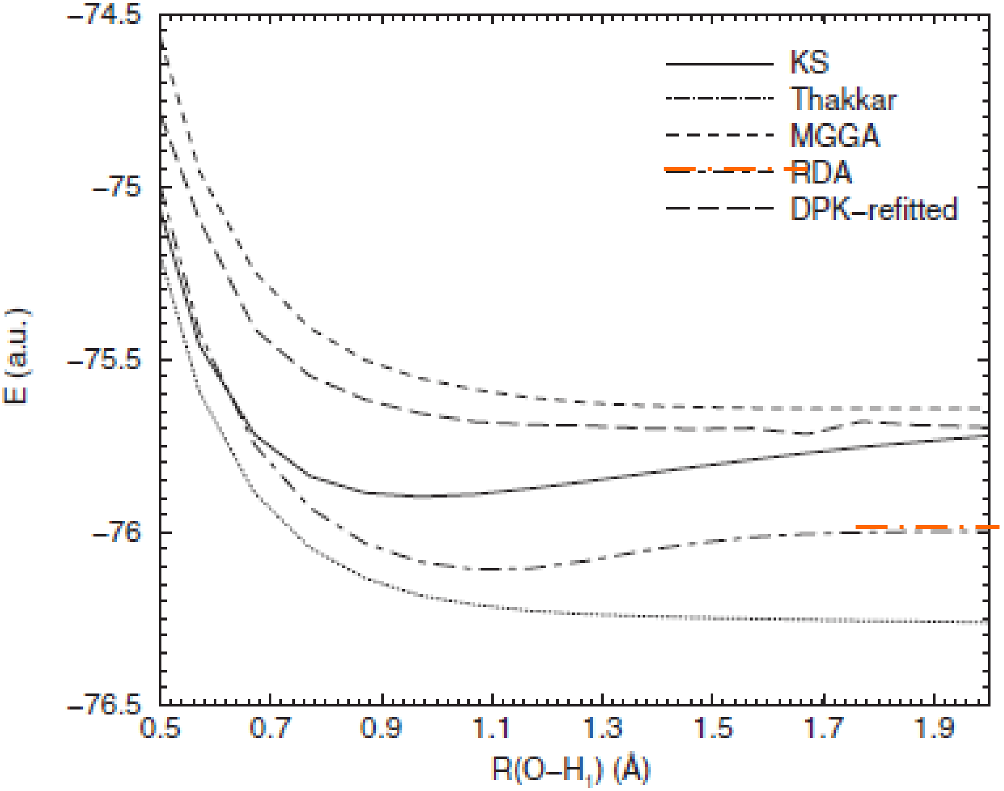
Even a numerical grid diatomic molecule code is slow to converge and unpredictable.

Comput. Phys. Commun. (submitted)

OF-DFT - Removing Pauli Potential Singularities

Current work is to remove mcGGA singularities by partial resummation of gradient expansion to respect Kato cusp condition. One functional has been explored a little.

H_2O molecular *total energy*
as function of one bond
KS = reference calc (source of
input density; middle curve)
DPK = DePristo-Kress OFKE
functional reparameterized
for this case (2^{nd} from top)
MGGA = meta-GGA functional of
Perdew and Constantin (top)
Phys. Rev. B 75, 155109 (2007).
Thakkar functional (lowest curve)
RDA = This work (second lowest)



Phys. Rev. B 80, 245120 (2009)

Confined System – finite-T Hartree-Fock

- **The model problem is a hard-walled rectangular parallelepiped containing a few (1-8 for now) hydrogen atoms.**
- **Initial exploration with cubic box, edge-length L.**
- **A few fixed atomic positions are sampled.**
- **Box size is from 1 au^3 (L = 1 au) to free-system limit ($L \to \infty$).**
- **Temperature range: $0 \le T \le 200{,}000$ K.**

Basis Set – Confined System

Requirements:

- **Match boundary conditions.**
- **Represent ground state and sufficient number of excited states at different box sizes.**
- **Allow for efficient calculation of 2-electron integrals.**

Basis:

Cartesian Gaussians truncated to match BCs.

Coefficients a_0, a_L set by requiring each basis function to be continuous.

$$g_{box}^{n}(x) := a_0\left(g^n(x;x_c) - \Delta_0\right) \quad 0 \le x \le x_c$$

$$:= a_L\left(g^n(x;x_c) - \Delta_{L_x}\right) \quad x_c \le x \le L_x$$

$$\Delta_0 := g^n(0) \quad ; \quad \Delta_{L_x} := g^n(L_x)$$

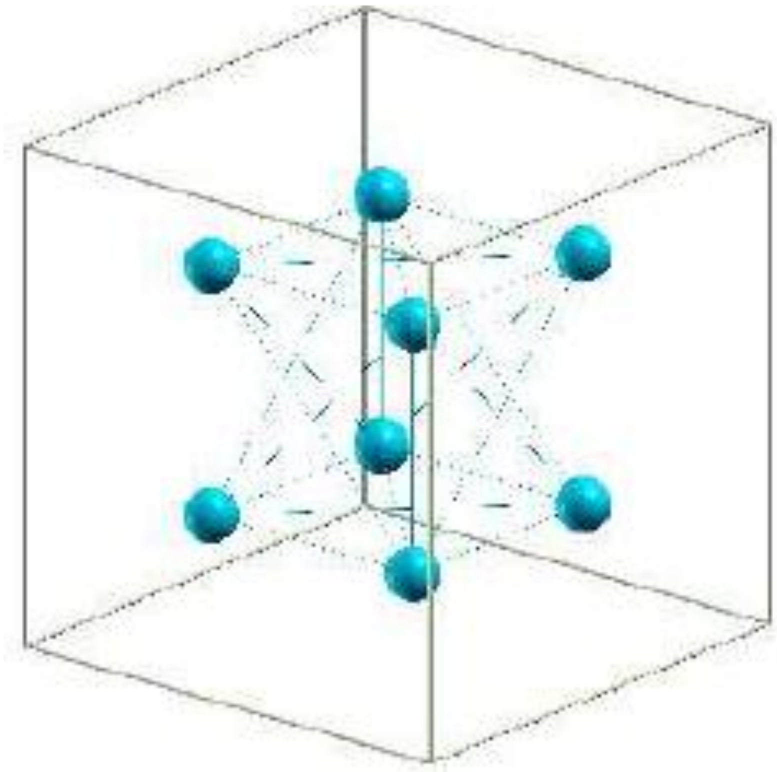
$$g^n(x;x_c) = (x - x_c)^n e^{-\alpha(x-x_c)^2}$$

Basis Set - continued

Technical issues and resolution:

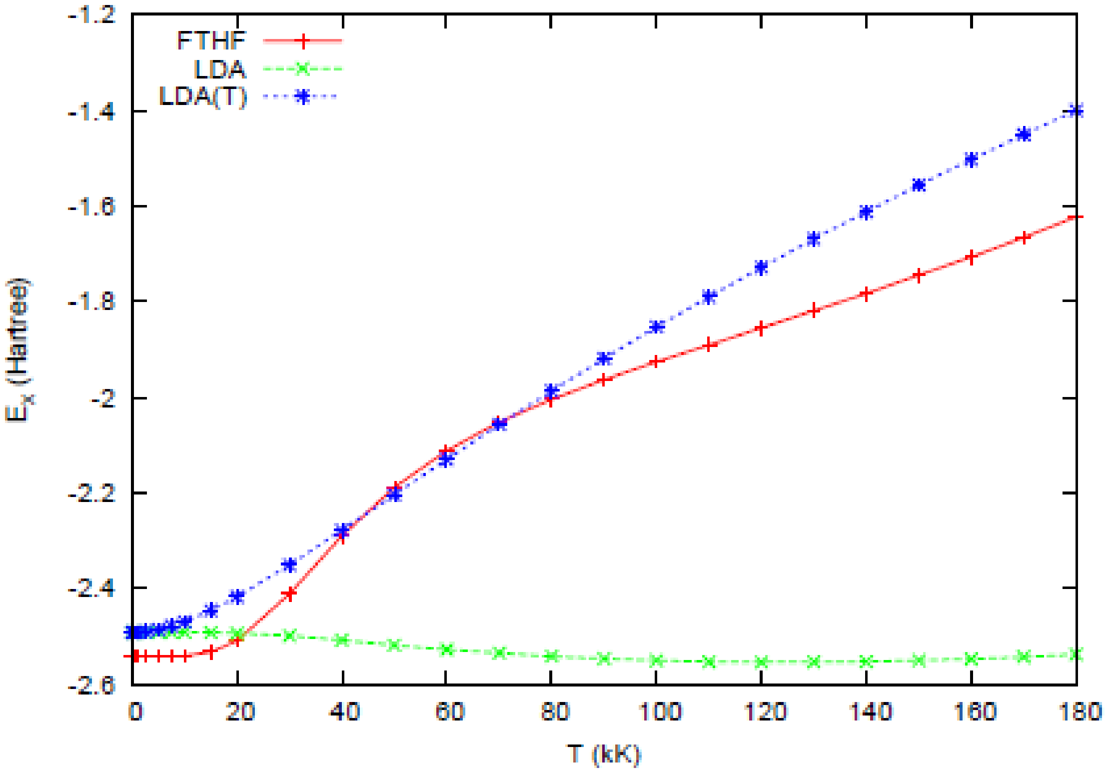
- **Continuity of first derivative at matching point and corrections to piecewise evaluation of KE matrix elements – works with a non-zero piece-wise correction for p-type functions**
- **Efficient calculation of 2- electron integrals – finite-range integrals of Gaussians and error functions done analytically as much as possible, rest via Gauss-Legendre quadrature.**

Results – 8 Atom Array of Cubical Symmetry in a Cubical Box



The ion configuration. Each ion is at the center of its own octant. (An initial choice for exploration. In general, the ion configuration is arbitrary.)

Comparison of Exchange Functionals



E_x from finite-temperature Hartree-Fock (FTHF)

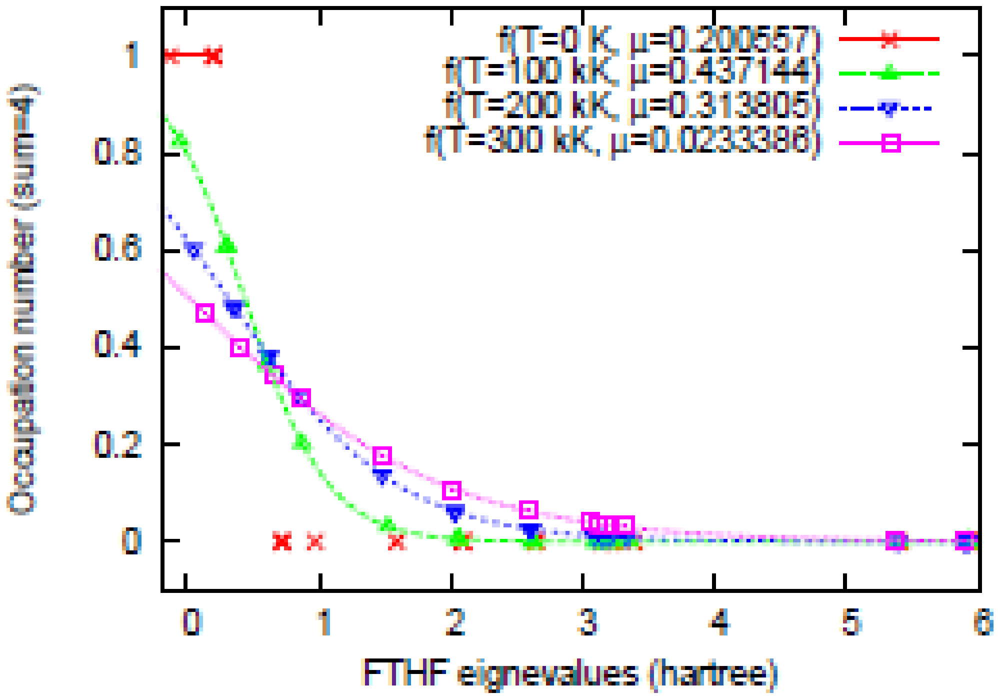
E_x from ground state LDA with FTHF density $E_x(T) = \left(-3\sqrt[3]{3\pi^2}/4\pi\right)\int d\mathbf{r}\, n^{4/3}(\mathbf{r},T)$

E_x from temperature-dependent LDA (Perrot & Dharma-Wardana 1984 parameterization) with FTHF density.

All for 8 atoms, cubic symmetry, in cubic box, L = 6 bohr

Phys. Rev. B 85, 045125 (2012)

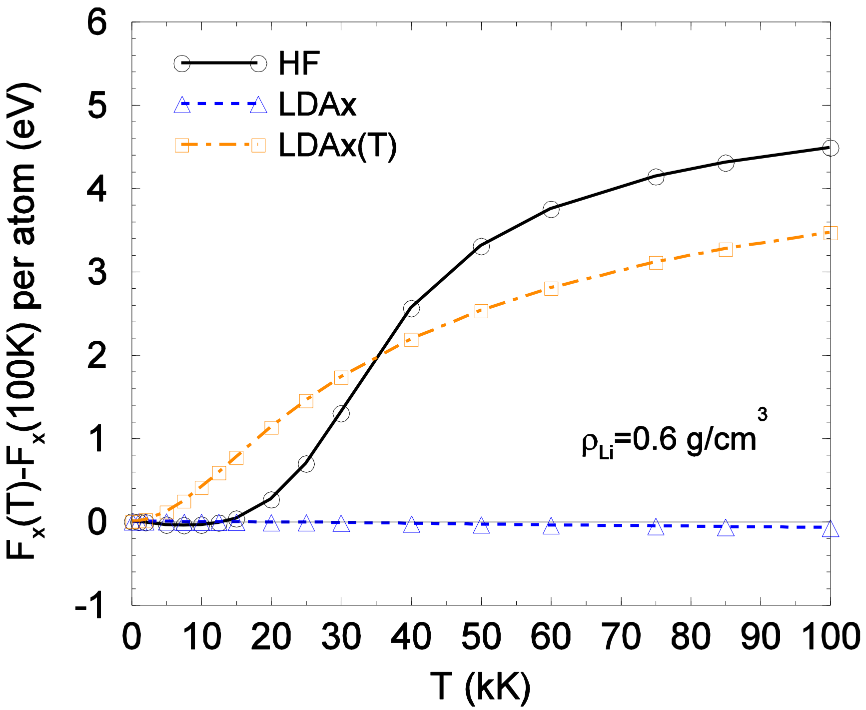
8 Atom Cubical Array – Low-T plateaus?

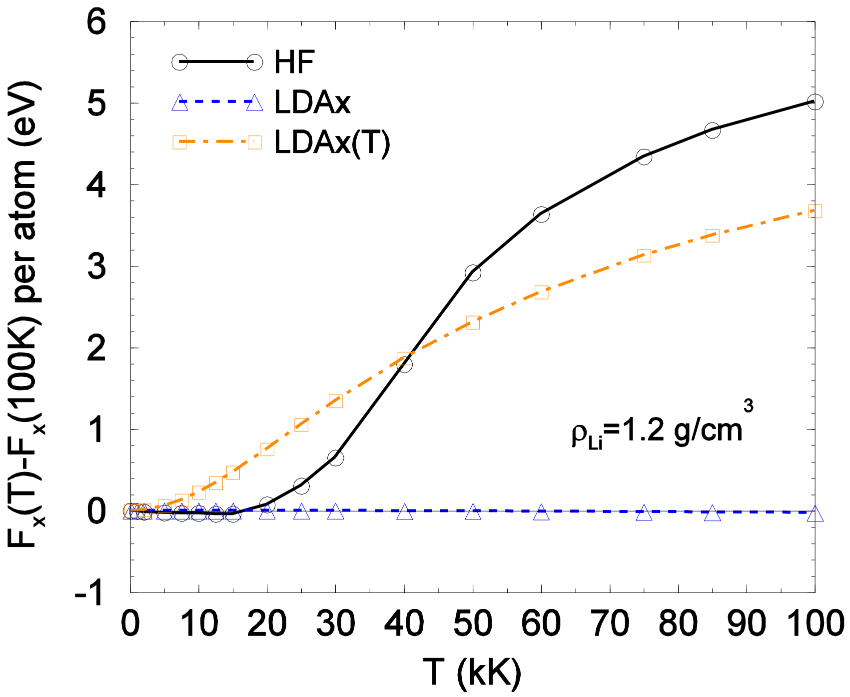


Fermi distribution for a single spin for four temperatures at *L* = 6 bohr. Note that the *T*=0 K occupied orbitals induced by cubic symmetry are a single *a1g* and a triply degenerate *t1u*.

Finite-T Hartree-Fock, LDAx, LDAx(T) Exchange free energy

Periodic bcc Lithium at ambient and 2x density. Modified AbInit code. (orbital-dependent, nor orbital free).

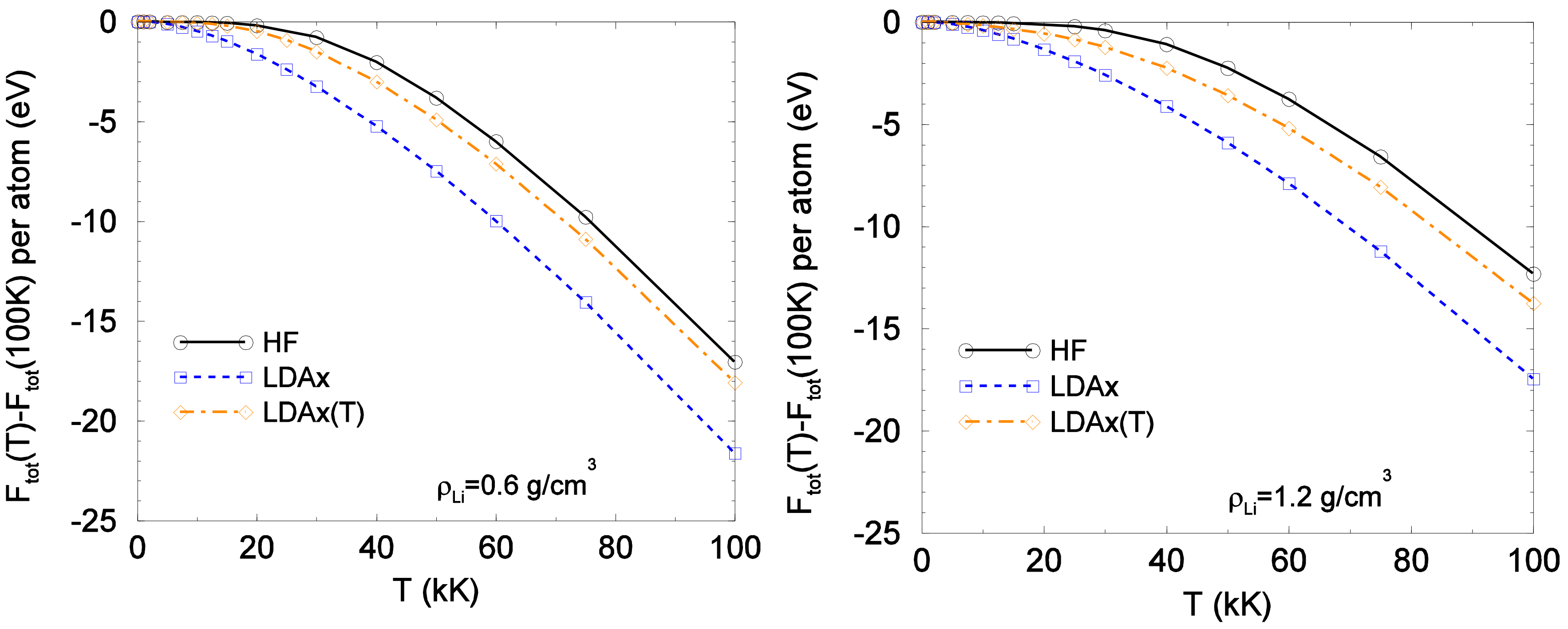




$\Delta F_X(T) = F_X(T) - F_X(T = 100\ K)$ per atom.

LDAx(T) is from Perrot and Dharma-Wardana, Phys. Rev. A 30, 2619 (1984).

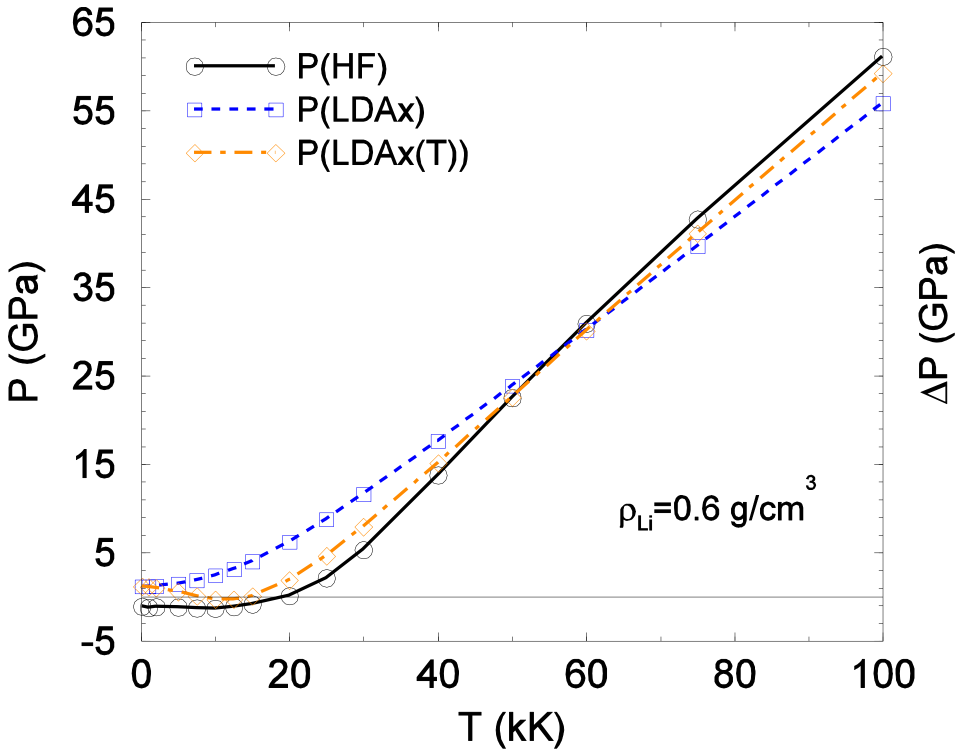
Finite-temperature Hartree-Fock, LDAx, LDAx(T) Total free energy

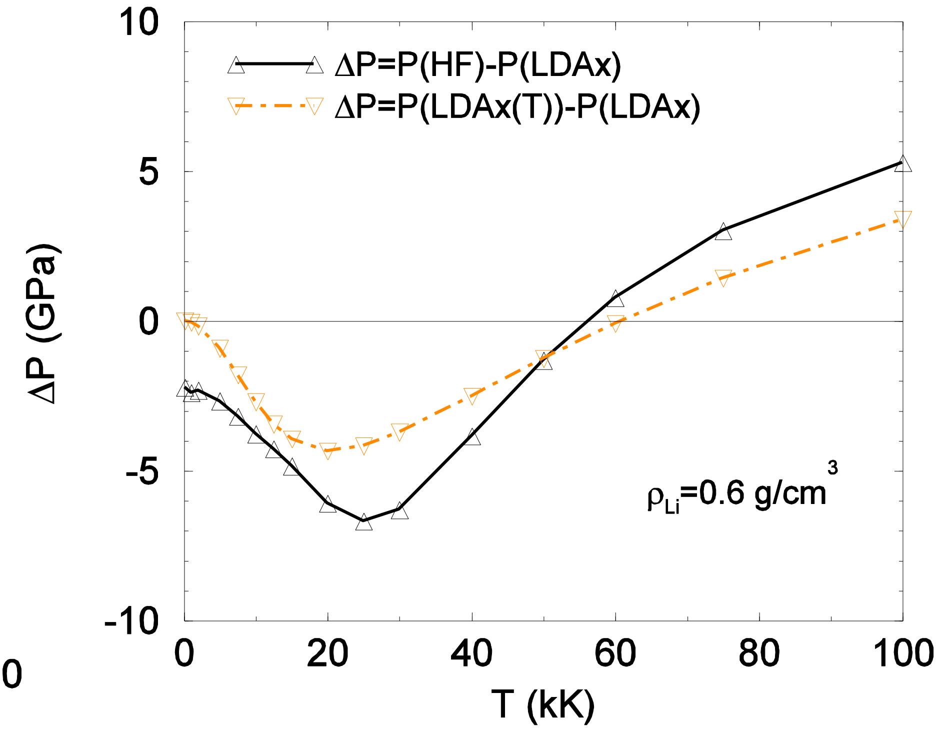


$\Delta F_{\text{total}}(T) = F_{\text{total}}(T) - F_{\text{total}}(T = 100\text{ K})$ per atom.
LDAx(T) is from Perrot and Dharma-Wardana, Phys. Rev. A <u>30</u>, 2619 (1984).

Periodic bcc Lithium at ambient and 2x density.
Modified AbInit code (orbital dependent, not orbital-free).

Finite-temperature Hartree-Fock, LDAx, LDAx(T) Eq. of State: ρ=0.6 g/cm³





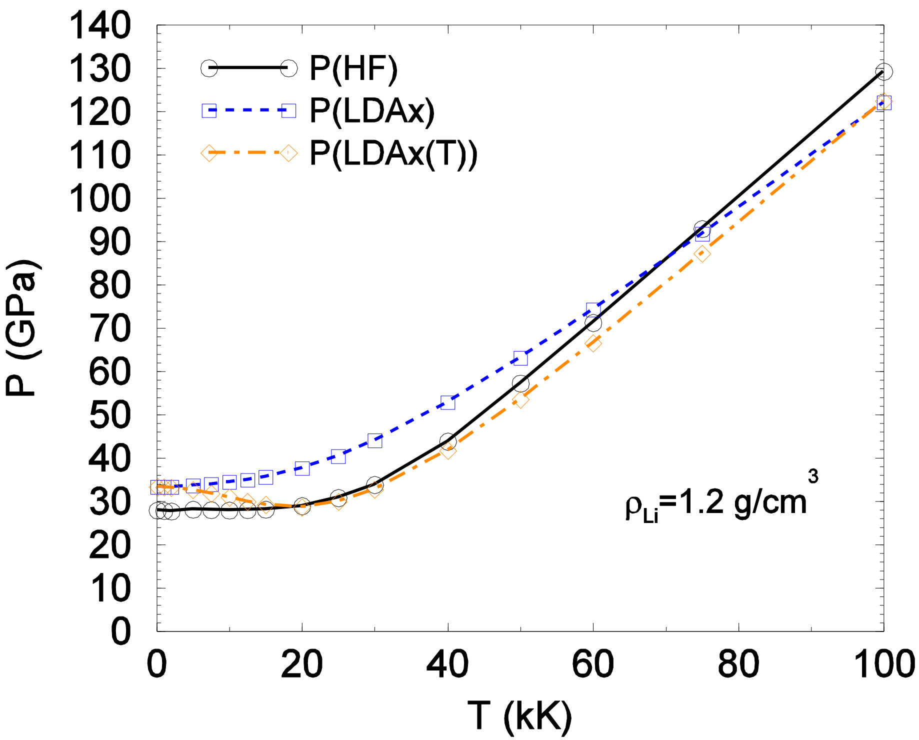
Pressure vs T: HF, LDAx, LDAx(T)

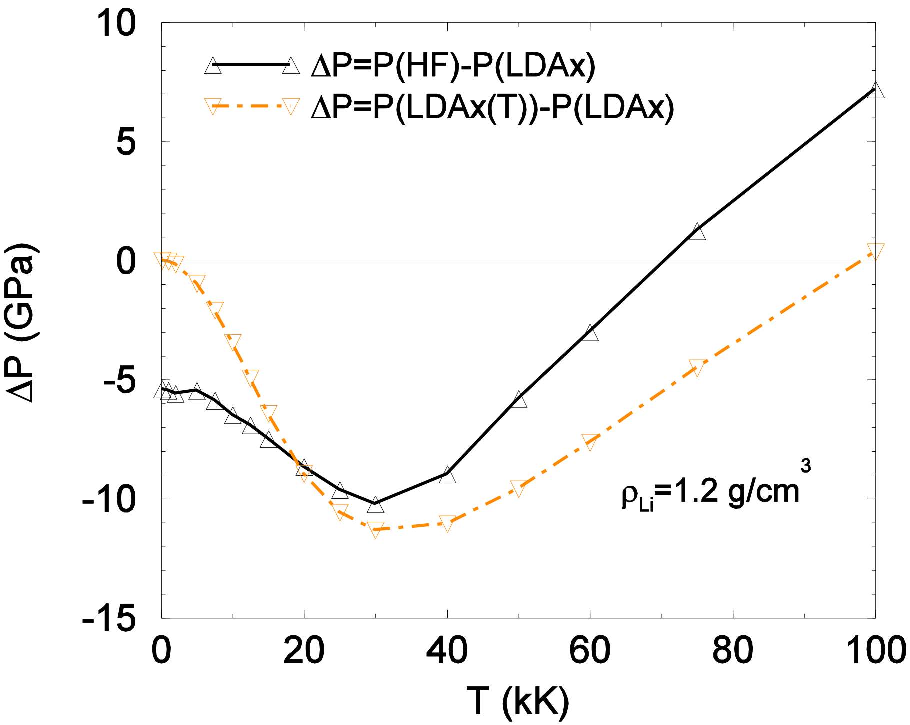
$$\Delta P(T) = P_{HF}(T) - P_{LDAx}(T);$$

$$\Delta P(T) = P_{LDAx(T)}(T) - P_{LDAx}(T)$$

Bcc Lithium at ambient density. Modified AbInit code (orbital dependent, not orbital-free).

Finite-temperature Hartree-Fock, LDAx, LDAx(T) Eq. of State: ρ=1.2 g/cm^3





Pressure vs T: HF, LDAx, LDAx(T)

$$\Delta P(T) = P_{HF}(T) - P_{LDAx}(T);$$

$$\Delta P(T) = P_{LDAx(T)}(T) - P_{LDAx}(T)$$

Bcc Lithium at 2 x ambient density. Modified AbInit code (orbital-dependent, not orbital-free.

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