UF UNIVERSITY of FLORIDA

The Quantum Theory Landscape for Warm Dense Matter

Sam Trickey

Quantum Theory Project
Physics, Chemistry - University of Florida

Workshop IV, IPAM Long Program
21 May 2012

Funding: **U.S. DoE DE-SC 0002139**

http://www.qtp.ufl.edu/ofdft
trickey@qtp.ufl.edu

Outline

A] Ultra-rapid Tour of *Ultra-simple* Stuff (level set)

B] Short Survey - Relevant Ground-state QM methods

C] Quantum Statistical Mechanics Methods in Current Use
[and some issues with those methods]

D] A Current Research Interest

To Begin

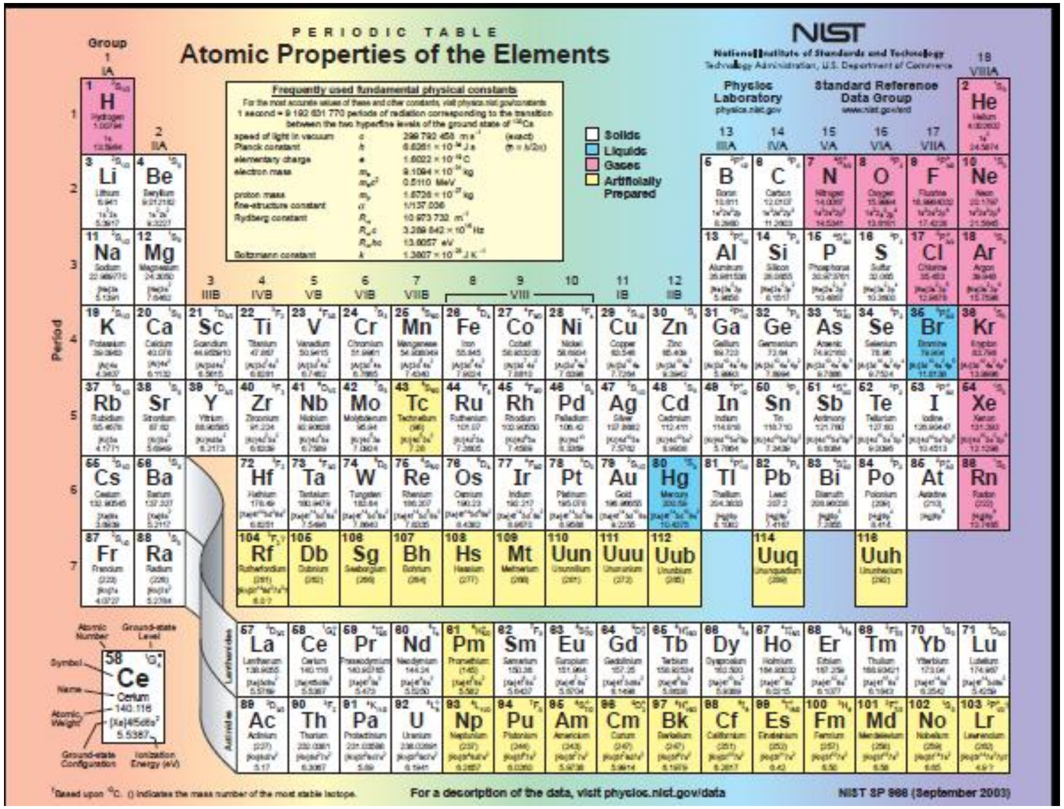
DISCLAIMER: Can’t cover everything in this topic!

THANKS – BUT NO BLAME – TO

U. Florida Orbital-free DFT Group:
Jim Dufty, Támas Gál, Frank Harris, Valentin Karasiev, Keith Runge, Travis Sjostrom

Mexican DFT Collaboration:
José Luis Gázquez, Jorge Martín del Campo, Alberto Vela

Ultra-simple Stuff
QM determines material properties



PERIODIC TABLE

Atomic Properties of the Elements

NIST

Physics Laboratory

Standard Reference Data Group

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

No QM → No periodic table

No periodic table → no chemistry, no materials specificity

But WDM involves H, He, Li, C, H_2O, …

Ultra-simple Stuff:
Lengths & Ratios relevant to WDM

$$\left.\begin{aligned}\Gamma &= \frac{\langle PE \rangle}{\langle KE \rangle} \approx 1 \\ \Theta_F &= \frac{E_F}{k_B T} \equiv \beta E_F \approx 1\end{aligned}\right\}$$

No small parameter →
No perturbation treatment

Thermal de Broglie wavelength

for electrons (m_e= electron mass)

$$\Lambda_e := \left(\frac{2\pi\beta\hbar^2}{m_e} \right)^{1/2}$$

Ultra-simple Stuff:
Units relevant to WDM

Hartree atomic units

$$\hbar = m_e = q_e = 1$$

$$1\,\mathrm{E}_{Hartree} = 27.2116\ \mathrm{eV} \quad ; \quad 1\ \mathrm{bohr} = 0.5292\ \text{Å}$$

$$\text{One-electron KE:} - {}^{1}\!/_{2} \int d\mathrm{r}\, \phi \nabla^2 \phi$$

1 Hartree au , pressure:

$$1\mathrm{E}_{Hartree} \,/\, \mathrm{bohr}^3 = 294.2\,\mathrm{Mbar}$$

$$= 0.2942\ \mathrm{Tbar}$$

1 Hartree au, magnetic field:

$$1 B_{Hartree} = 2.35 \times\ 10^5\,\mathrm{Tesla}$$

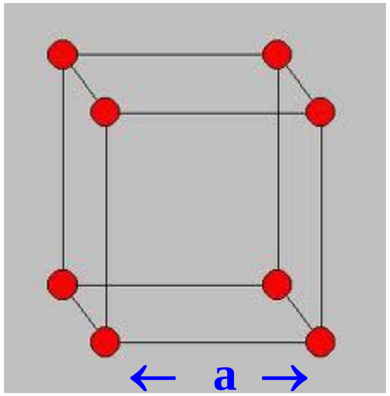
Ultra-simple Stuff
Lengths & Ratios relevant to WDM

Simple cubic H at 1 g/cm^3

(≈ 1.8 compression)

Lattice parameter: a = 2.24 au

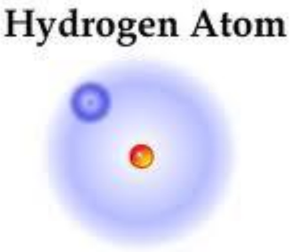
T_e (K)	Λ_e (au)
100	140.9
10^4	14.09
10^5	4.45
10^6	1.41



← Λ_e(T=10^5 K) ≈ 2a →

Even at T=10^5 K , the electron is effectively about twice the size of the cube edge! QM for the electrons is unavoidable.

Ultra-simple Stuff
Simplest QM models – H atom



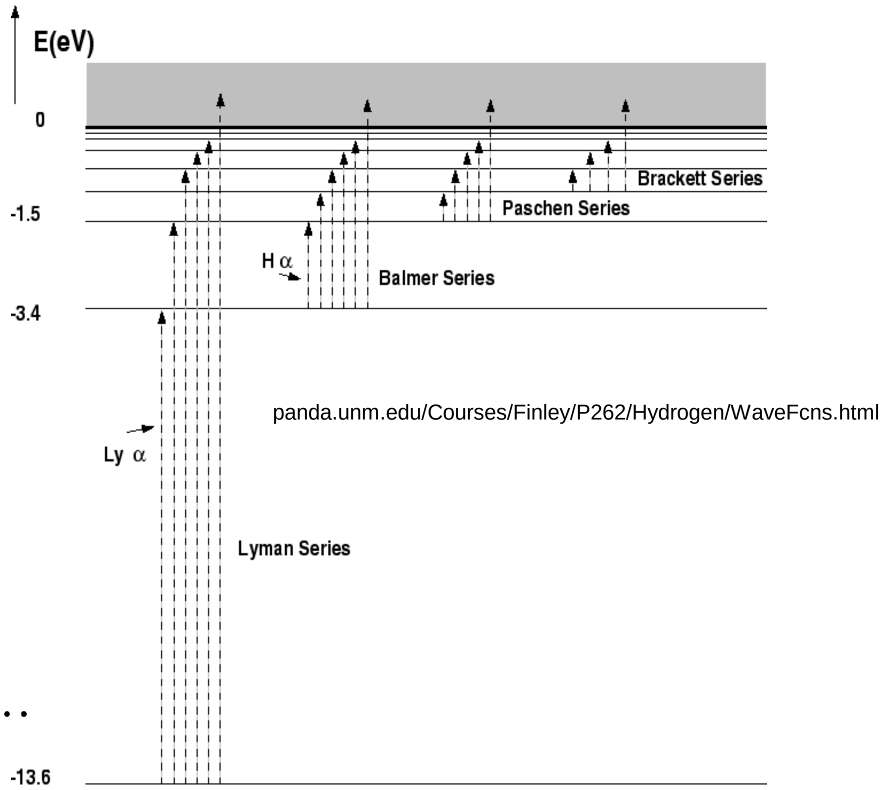
Basic H atom eqns:

$$\hat{H}\chi_{nlm} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\chi_{nlm} = \varepsilon_{nlm}\chi_{nlm}$$

$$\varepsilon_{nlm} = -\frac{1}{2n^2} + \text{fine structure corrections;} \qquad n = 1, 2, \cdots$$

$$\chi_{nlm} = c_{nl} e^{-2r/n} \left(\frac{2r}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right) Y_l^m(\vartheta, \varphi)$$

Note: vacuum boundary conditions



panda.unm.edu/Courses/Finley/P262/Hydrogen/WaveFcns.html

Paradigm for spectroscopy

Ultra-simple Stuff
Simplest QM models – Particle in a box

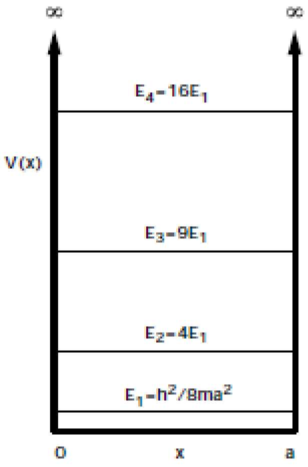
Basic 1D particle in box eqns:

$$\hat{H}\psi_n = \left(-\frac{1}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi_n = \varepsilon_n\psi_n$$

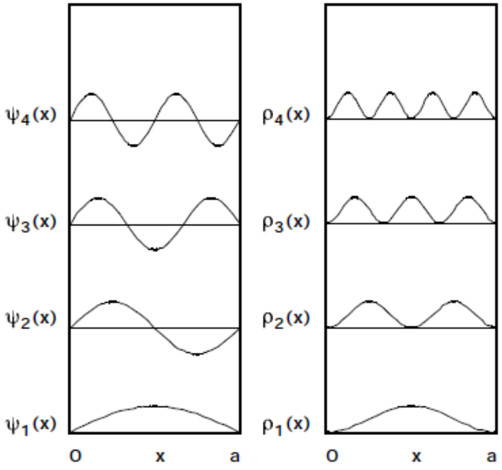
$$V(x) = 0,\ 0 \le x \le a;\ V(x) = \infty, \forall \text{other } a$$

$$\varepsilon_n = \frac{1}{2m}\left(\frac{n\pi}{a}\right)^2 \equiv \frac{k_n^2}{2m};\ n = 1, 2, \ldots$$

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin(k_n x),\ 0 \le x \le a; \quad \text{otherwise zero}$$



spectrum

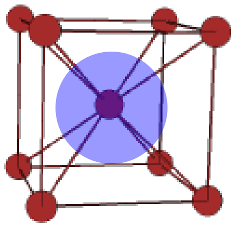


Eigenfns and prob. densities

www.umich.edu/~chem461/QMChap3.pdf

Ultra-simple Stuff
Simplest QM models – Homogeneous Electron Gas

HEG eqns:

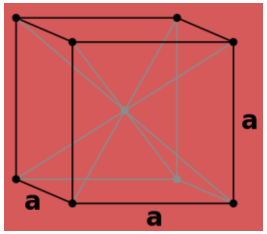


$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \bar{n}\int d\mathbf{r}_1 dR\,\frac{n(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{R}|} + \frac{1}{2}\bar{n}^2\int d\mathbf{r}_1 d\mathbf{r}_2\,\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$\downarrow$

Non-interacting case (energy per electron)

$$E = \mathcal{T} = \frac{3}{10}k_F^2 \quad ; \quad k_F := (3\pi^2)^{1/3} n^{1/3} = \left(\frac{9}{4\pi}\right)^{1/3}\frac{1}{r_s}$$



$\bar{n}$

Include exchange (energy per electron)

$$E = \frac{1.105}{r_s^2} - \frac{0.458}{r_s}$$

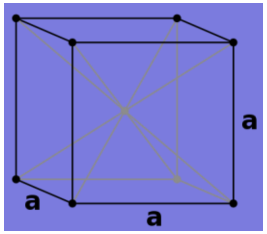
$$r_s := \left(\frac{3}{4\pi}\right)^{1/3} n^{-1/3}$$

Uniformly smeared nuclei

$+$

Also include correlation (energy per electron)

$$E = \frac{1.105}{r_s^2} - \frac{0.458}{r_s} - 0.048 + O(r_s) \quad \text{for small } r_s$$



Uniformly smeared electrons

Many-electron Hamiltonian and Born-Oppenheimer Approximation

Born-Oppenheimer Approximation: N_e-electrons in the field of N nuclei at positions {R}

$$\hat{\mathcal{H}}(\{\mathbf{R}\},\mathbf{r}_1,\ldots\mathbf{r}_{N_e}) = \hat{\mathcal{H}}_{NN}(\{\mathbf{R}\}) + \hat{\mathcal{H}}_{\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)$$

$$\hat{\mathcal{H}}_{NN}\left(\{\mathbf{R}\}\right) = -\frac{1}{2m_N}\sum_{I=1}^{N}\nabla^2_{\mathbf{R}_I} + \frac{1}{2}\sum_{I,J}^{N}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

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

$$:= \hat{\mathcal{H}}_{e\{\mathbf{R}\}}\left(\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right) + \hat{V}_{ext}\left(\{\mathbf{R}\};\mathbf{r}_1,\ldots\mathbf{r}_{N_e}\right)$$

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

Born-Oppenheimer MD – ion forces from gradient w/r ion coordinates of ground state "potential surface"

$$\mathbf{F}_I = -\nabla_I\left\{\frac{1}{2}\sum_{J,K}^{N}\frac{Z_J Z_K}{|\mathbf{R}_J - \mathbf{R}_K|} + \mathcal{E}_{0;\{\mathbf{R}\}}\right\}$$

T=0 K QM: Hartree-Fock Approximation

Simplest physically acceptable approximate wave function is *H*artree-*F*ock → trial variational determinantal wave-function:

$$\underbrace{\psi(1,2,\ldots,N_e)}_{\text{Fully coupled electrons}} \approx \underset{\text{Antisymmetrizer}}{\mathcal{A}}\underbrace{\left[\overset{\text{Spin-orbital}}{\varphi_a}(1)\,\varphi_b(2)\cdots\varphi_z(N_e)\right]}_{\text{Forced separation of variables = “mean field”}}$$

Another shorthand notation: $1 \rightarrow \mathbf{r}_1, \sigma_1$

$$\left\{-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{\left|\vec{r}_i - \vec{R}_I\right|} + \int d\vec{r}_2 \frac{n_{HF,\{\vec{R}\}}(\vec{r}_2)}{\left|\vec{r}_1 - \vec{r}_2\right|}\right\}\varphi_j\left(\vec{r}_1,\sigma_1;\left\{\vec{R}\right\}\right)$$

Orbital optimization for variational minimum

$$-\sum_{i=1}^{N}\delta_{m_i,m_j}\left[\int d\vec{r}_2 \frac{\phi_i^*\left(\vec{r}_2,\sigma_2;\left\{\vec{R}\right\}\right)\phi_j\left(\vec{r}_2,\sigma_2;\left\{\vec{R}\right\}\right)}{\left|\vec{r}_1 - \vec{r}_2\right|}\right]\varphi_i\left(\vec{r}_1,\sigma_1;\left\{\vec{R}\right\}\right) = \varepsilon_j\,\varphi_j\left(\vec{r}_1,\sigma_1;\left\{\vec{R}\right\}\right)$$

$$n_{HF,\{\vec{R}\}}(\vec{r}) = \sum_{i,\sigma}^{n}\left|\varphi_i\left(\vec{r},\sigma;\left\{\vec{R}\right\}\right)\right|^2$$

SCF solution

T=0 K QM: Hartree-Fock Interpretation & Koopmans' theorem

The Ionization Potential (energy to remove least-bound electron to infinity) is approximately related to the HF eigenvalue spectrum by:

$$I := E_{N_e - 1} - E_{N_e} \approx -\varepsilon_{HOMO}$$

"HOMO" = highest occupied molecular orbital = the highest occupied HF one-particle energy level.

This result is approximate because it assumes

a) "frozen orbitals" – the one-particle states of the ionized system are the same as in the ground state

b) the validity of the single-determinant wave function (no correlation)

Anticipatory warning: Koopmans' theorem does not hold for Kohn-Sham DFT eigenvalues.

HF characteristic – "HOMO-LUMO" gap

$$\varepsilon_{HLgap} = \left| \varepsilon_{HighestOccupiedMolecularOrbital} - \varepsilon_{LowestUnoccMolecularOrbital} \right|$$

usually overestimates the fundamental gap $\varepsilon_{gap} = I - A$

***A*= electron affinity**

T=0 K QM: Configuration Interaction

CI is a linear combination of singly, doubly, triply, etc. “excited” determinants with the coefficients determined variationally :

$$\psi_{CI}\left(1,2,\ldots,N_e\right) := \sum c_j D_j(1\cdots N_e)$$

$$\equiv c_0\mathcal{A}\left[\varphi_a(1)\varphi_b(2)\cdots\varphi_z(N_e)\right]$$

$$\textit{“excited” Slater determinants}\left\{\begin{array}{l} +c_1\mathcal{A}\left[\varphi_A(1)\varphi_b(2)\cdots\varphi_z(N_e)\right] \\ +c_2\mathcal{A}\left[\varphi_a(1)\varphi_B(2)\cdots\varphi_z(N_e)\right] \\ +\ldots+c_{N_e}\mathcal{A}\left[\varphi_a(1)\varphi_b(2)\cdots\varphi_Z(N_e)\right] \\ +c_{N_e+1}\mathcal{A}\left[\varphi_A(1)\varphi_B(2)\cdots\varphi_z(N_e)\right]+\ldots \end{array}\right.$$

Phase relationships between determinants *D*D_j enter in expectation values, e.g. the variational total energy:

$$\mathcal{E}_0 \le \mathcal{E}_{trial} = \left(\int \Psi^*_{CI}\Psi_{CI}\,d\mathbf{r}_1\ldots d\mathbf{r}_{N_e}\right)^{-1}\left\{\ldots+c_j^*c_k\int D_j^*\hat{\mathcal{H}}D_k\,d\mathbf{r}_1\ldots d\mathbf{r}_{N_e}+\ldots\right\}$$

CI is not the same as an ensemble average

T=0 K QM: Multi-Configuration SCF

- **CI is computationally expensive.**
- **Picking truncations of it can lead to anomalies (size consistency problems). There is a cottage industry of "active space" methods for this.**
- **A variational trial function which is a sum of several configurations and optimized orbitals can be useful. This is "multi-configuration self-consistent field". A trivial 3-term example would be**

$$\begin{aligned}\psi_{MCSCF}\left(1,2,\ldots,N_e\right) = {} & c_A D_A[\varphi_{A_1}(1)\cdots\varphi_{A_{N_e}}(N_e)] \\ & + c_B D_B[\varphi_{B_1}(1)\cdots\varphi_{B_{N_e}}(N_e)] \\ & + c_C D_C[\varphi_{C_1}(1)\cdots\varphi_{C_{N_e}}(N_e)]\end{aligned}$$

- **The MCSCF Euler equation looks like HF with many more orbitals.**
- **The physics is in picking which orbital types (symmetries) to include.**
- **For WDM, this scheme is most relevant to computing accurate *T=0* K atomic spectra. [Example: S.B. Hansen *et al.* , High En. Dens. Phys. 3, 109 (2007), which uses Gu's FAC code; see Can. J. Phys. 86, 675 (2008)]**

T=0 K QM: Density Functional Theory - basics

Hohenberg-Kohn Theorems: The ground state of an N_e electron system in an external potential v_{ext} is determined by the ground state density n_0. That density can be found from a universal (independent of v_{ext}) variational functional of the density alone.

Remark: In principle this is much cheaper than CI or MCSCF or even HF. But how does one get from the HK existence theorems to a workable scheme?

Start with some clever rearrangement (Kohn-Sham strategy) :

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

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

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

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

Non-interacting system orbitals

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

$$n(\mathbf{r}) \equiv \sum_{j=1} f_j \left| \varphi_j(\mathbf{r}) \right|^2 ; \quad f_j = 0,1, \text{ or } 0,1,2$$ (depending on spin treatment)

T=0 K QM: Density Functional Theory – KS eqns

For a non-interacting system (KS system) with the same density and μ

$$E_{KS}[n] = \mathcal{T}_S[n] + \int d\mathbf{r}\, n(\mathbf{r})\, v_{KS}(\mathbf{r})$$

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

Original system's Euler equation:

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

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

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

$$v_{ee}(\mathbf{r}) = \int d\mathbf{r}'\, n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$$

Comparison gives $v_{KS}(\mathbf{r}) = v_{ee}(\mathbf{r}) + \dfrac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r})$

And the famous KS eqns are:

$$\left\{-\nabla^2 + v_{KS}(\mathbf{r})\right\}\varphi_j = \varepsilon_j \varphi_j \quad ; \quad n(\mathbf{r}) \equiv \sum_{j=1} n_j \left|\varphi_j(\mathbf{r})\right|^2$$

T=0 K QM: DFT – some relevant facts

- **The KS eigenvalues obey the Slater- Janak thm (not Koopmans') -** $\varepsilon_j = {\partial E_{KS}}\big/{\partial n_j}$

- **IP Theorem – For the exact XC functional** $I = -\varepsilon_{HOMO}$

- **Explicit approx. *E*$_{xc}$ functionals (Local density approx., Generalized gradient approx., meta-GGAs) either do not correct for self-spurious self-repulsion at all or inadequately. The IP Theorem is not satisfied and "HOMO-LUMO" gap**

$$\varepsilon_{HLgap} = \left| \varepsilon_{HighestOccupiedMolecularOrbital} - \varepsilon_{LowestUnoccMolecularOrbital} \right|$$

usually is a poor approximation (30-50% too small) to the fundamental gap, *I*-*A*.

T=0 K QM: DFT– more relevant facts

• A related consequence is that eigenvalue differences from such functionals used in many-body expressions typically are too small.
Schematically:

$$K_1(\omega) = \sum_{j,k} \frac{\left| \left\langle \varphi_j \middle| \hat{O} \middle| \varphi_k \right\rangle \right|^2}{\varepsilon_j - \varepsilon_k - \omega}$$

$$K_2(\omega) = \sum_{j,k} \left| \left\langle \varphi_j \middle| \hat{O} \middle| \varphi_k \right\rangle \right|^2 \delta\left(\varepsilon_j - \varepsilon_k - \omega\right)$$

• Moreover, the KS orbitals are constrained to construct the density and minimize the KE operator expectation. They also <u>define</u> the DFT exchange energy. That’s all (But see Görling-Levy pert. theory.)

DFT details: Tutorial week lectures by Kieron Burke and SBT; talks this week by H. Gross, K. Burke, S. Pittalis, A. Mattsson

Quantum Statistical Mechanics - intro

Grand canonical ensemble

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

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

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

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

Features to notice:

1] Variational principle goes from $\langle\psi|\hat{O}|\psi\rangle$ **to** $\mathrm{Tr}\,\hat{O}$ **.**

2] Often this correspondence is a good heuristic for thinking about finite *T* expressions in terms of something familiar at *T* = 0 K.

3] The boundary conditions on Ψ_i **in the Tr are not stated but are essential to the description of any problem.**

4] In the grand ensemble, the particle number N_e **is the average determined by** μ

5] Unlike CI or MCSCF, phase relations between states don't enter in ensembles

$$\bar{O} = \sum_i w_i \langle\psi_i|\hat{O}|\psi_i\rangle \quad ; \quad \sum_i w_i = 1$$

Quantum Stat. Mech. : finite-T BOMD

$$\mathbf{F}_K = -\nabla_K \left\{ \frac{1}{2} \sum_{I \neq J}^{N} \frac{Z_I Z_J}{\left| \mathbf{R}_I - \mathbf{R}_J \right|} + \mathcal{F}\left(\left\{ \mathbf{R} \right\}, T \right) \right\}$$

↑

Many-electron Free-energy in field of nuclei fixed at {R}

Quantum Stat. Mech. Example: finite-T Hartree-Fock - I

Finite Temperature Hartree-Fock (ftHF) approximation = "obvious" generalization of *T*=0 *K* HF [Mermin, Ann. Phys. (NY) <u>21</u>, 99 (1963)]. The essence is restriction of traces to the space of N_e-electron Slater determinants.

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

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

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

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

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

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

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

Trace "N_e,*SD*" is over complete set of N_e-electron Slater determinants.

Quantum Stat. Mech. Example: finite-T Hartree-Fock - II

Variational extremalization → expected generalization of the T=0 K HF equation:

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

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

Quantum Stat. Mech.: finite-T DFT - I

Mermin [Phys. Rev. 137, A1441 (1965)]; in Hartree au as usual

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

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

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

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

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

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

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

Again: notice close parallel with *T = 0* K theory, here DFT

$$E_{ion-e}[n] = \int d\mathbf{r}\, n(\mathbf{r}) v_{ion-e}(\mathbf{r})$$

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

UNIVERSITY of FLORIDA

Quantum Stat. Mech.: ftDFT - II

Euler equation for the density now involves

$$v_{xc}(\mathbf{r}) = \frac{\delta \mathcal{F}_{xc}}{\delta n(\mathbf{r})}$$

$$v_{ee}(\mathbf{r}) = \int d\mathbf{r}'\, n(\mathbf{r}') / |\mathbf{r}-\mathbf{r}'|$$

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

Again $v_{KS}(\mathbf{r}) = v_{ee}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})$

And the KS eqns are of same form:

$$\left\{-\nabla^2 + v_{KS}(\mathbf{r})\right\}\varphi_j = \varepsilon_j \varphi_j$$

Remarks:

- **$v_{ion\text{-}e}$ shown (prev. slide) as the bare Coulomb nuclear-electron interaction, but it could be an ionic Coulomb-electron interaction. For either, a plane-wave basis requires regularization (pseudo-potential).**
- **Everything except $\mathcal{F}_{xc}$ is known; it must be approximated. Much less known about finite-*T* approximations than *T=0* K approximate E_{xc} .**

Quantum Stat. Mech. Example: finite-T , Exact-exchange DFT

Finite-*T* exact-exchange Density Functional Theory in the Kohn-Sham context has the same structure as ft-HF <u>UNTIL</u> the variational minimization.

$$\Omega_{EXX}(\beta\,|\,\{\varphi\}) = -\beta^{-1}\ln\sum_{N_e=0}^{\infty}\mathrm{Tr}^{(N_e,SD)}e^{-\beta(\hat{\mathcal{H}}_e-\int d\mathbf{r}[\mu-v_{ion}(\mathbf{r})]n(\mathbf{r}))}$$

$$\mathcal{F}_{EXX}\left[\{\varphi[n]\}\right] = \mathcal{T}_S\left[\{\varphi[n]\}\right] - T\mathcal{S}_S[n] + E_{ee}\left[\{\varphi[n]\}\right] + E_x\left[\{\varphi[n]\}\right] + E_{ion}\left[n\right] + E_c$$

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

$$\mathcal{T}_s\left[\{\varphi[n]\}\right] := \tfrac{1}{2}\sum_j f_j\int d\mathbf{r}\left|\nabla\varphi_j(\mathbf{r})\right|^2 \quad ; \quad \mathcal{S}_s[n] := -k_B\sum_j\left[f_j\ln f_j + (1-f_j)\ln(1-f_j)\right]$$

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

$$E_x\left[\{\varphi\}\right] = -\frac{1}{2}\sum_{ij} f_i f_j\delta_{\sigma_i\sigma_j}\int d\mathbf{r}_1 d\mathbf{r}_2\,\frac{\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_2)\varphi_j^*(\mathbf{r}_2)}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}$$

EXX has a *LOCAL* Kohn-Sham potential, <u>NOT</u> the HF non-local X potential: $v_x(\mathbf{r}) = \dfrac{\delta E_x}{\delta n(\mathbf{r})}$

M. Greiner, P. Carrier, and A. Görling,
Phys. Rev. B <u>81</u>, 155119 (2010)
A. Görling., J. Chem. Phys. **<u>123</u>**, 062203(2005)

A. Görling's talk

Quantum Stat. Mech. Self-consistent Charge Tight-binding DFT

This method was in Predrag Krstić's Workshop II talk about the plasma-material interface. Usually the method is presented at *T=0* K but nothing prevents doing ftDFT as shown here.

Suppose a reasonable reference density $n_0(\underline{r})$ such that the actual density is a small perturbation: $n = n_0 + \delta n$. Furthermore, assume that only valence density variations are significant. Expand the DFT energy in powers of δn.

$$\mathcal{F}(\{\mathbf{R}\}) \approx \sum_{i}^{n/2} f_i \left\langle \phi_i \middle| \hat{h}_{KS,0} \middle| \phi_i \right\rangle + \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \delta n_{\{\mathbf{R}\}}(\vec{r}_1)\, \delta n_{\{\mathbf{R}\}}(\vec{r}_2) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \left. \frac{\delta^2 \mathcal{F}_{xc}}{\delta n \delta n} \right|_0 \right)$$

$$-\tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{n_{\{\mathbf{R}\},0}(\mathbf{r}_1)\, n_{\{\mathbf{R}\},0}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \mathcal{F}_{xc}[n_{\{\mathbf{R}\},0}] - \int d\mathbf{r}\, n_{\{\mathbf{R}\},0}(\mathbf{r})\, v_{xc}[n_{\{\mathbf{R}\},0}(\mathbf{r})] + \mathcal{F}_{core}$$

$$\hat{h}_{KS,0} \equiv -\tfrac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \int d\mathbf{r}_1 \frac{n_{\{\mathbf{R}\},0}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} + v_{xc}[n_{\{\mathbf{R}\},0}(\mathbf{r})]$$

Then come several semi-empirical procedures well-known in solid-state electronic structure and quantum chemistry. Summary on next slide.

M. Elstner et al.Phys. Rev. B 58, 7260 (1998)
M. Elstner *et al*., J. Comput. Chem. 24, 565 (2003)

Quantum Stat. Mech. Self-consistent Charge Tight-binding DFT - II

Essence of semi-empirical quantum chemistry and solid-state tight-binding schemes is to build the Hamiltonian matrix in a basis WITHOUT evaluating the matrix elements as explicit multi-dimensional integrals.

SCC-TBDFT semi-empirical procedures have some twists: a *localized* minimal basis, neglect of 3,4-center matrix elements, and parameterization of the remaining matrix elements.

$\phi_i = \sum_\mu b_{i,\mu}\chi_\mu$ basis of localized (Eschrig) atomic eigenfunctions

$\hat{h}^{\mu\mu}_{KS,0} \approx \varepsilon_{0,\mu}$ atomic eigenvalues; $h^{\mu\nu}_{KS,0} \approx \langle \mu_A | \hat{T} + V_{KS}[n_0^A] + V_{KS}[n_0^B] | \nu_B \rangle$

$\delta n \approx \sum_I \delta n_I$; $\delta n_I \approx q_I - q_{0,I} \equiv \Delta q_I$ atomic-site charges

q_I = Mulliken population, atom I

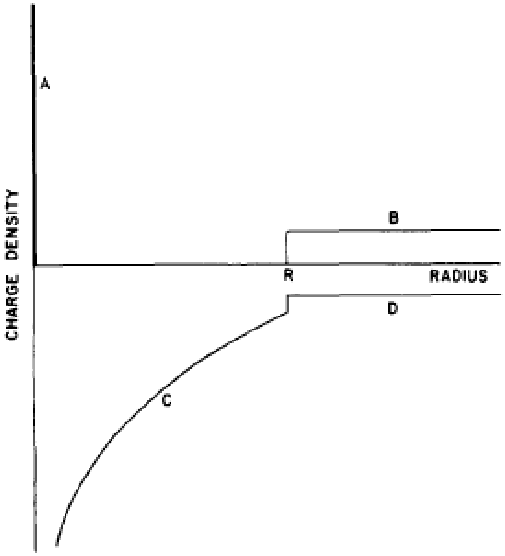
$q_{0,I}$ = number of valence electrons on I in ref. config.

$\left.\dfrac{\delta^2 \mathcal{F}_{xc}}{\delta n \delta n}\right|_0 \approx \gamma_{AB}$; γ_{AA} both from atomic prescriptions

$$\mathcal{F}_{SCTB}(\{\mathbf{R}\}) = \sum_i^{n/2} \langle \phi_i | \hat{h}_{KS,0} | \phi_i \rangle + \tfrac{1}{2} \sum_{I,J} \gamma_{IJ} \Delta q_I \Delta q_J + \mathcal{F}_{rep}(\{\mathbf{R}\})$$

$$\mathbf{F}_I = -\nabla_I \left\{ \mathcal{F}_{SCTB}(\{\mathbf{R}\}) + \frac{1}{2} \sum_{J,K}^{N} \frac{Z_J Z_K}{|\mathbf{R}_J - \mathbf{R}_K|} \right\}$$

Average Atom – Liberman's scheme



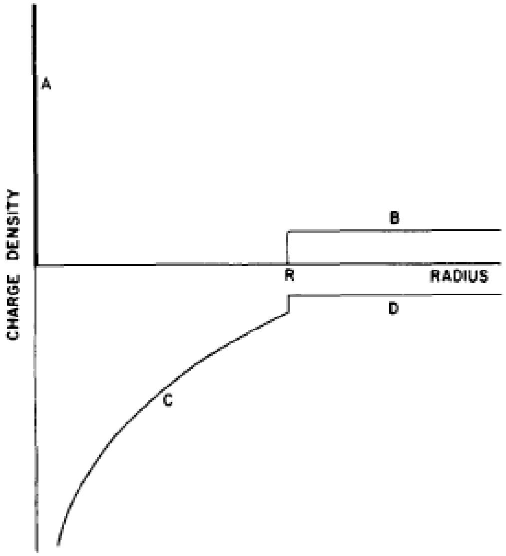
Kohn-Sham local density eignvalues for spectra? Ion radial distribution averaged away? (Ion-Ion interactions are gone.)

- **Single nucleus, charge *Z*, at origin.**
- **"Muffin –tin" potential and charge density inside sphere radius *R* ("C" in fig.).**
- **Charge neutrality inside sphere determines *R*.**
- **Jelium positive charge outside determines plasma density ("B" in fig.), which is modeled with HEG and matched to charge neutrality outside *R* ("D" in fig.). Ion distribution** $G(r) \approx \theta(r-R)$
- ***T= 0* K LDA for X (no C)**
- **Dirac KS eqns inside sphere with finite-*T* Fermi-Dirac occupations.**
- **Procedure for handling continuum states.**
- **Two prescriptions for ("T", "A") for separating atomic contributions.**
- **Prescription for interpolating to TFD at high *T* (10^7 K); this does not seem to be published.**

B. Wilson's talk?

INFERNO: D.A. Liberman, Phys. Rev. B 20, 4981 (1979)
PURGATORIO: B. Wilson *et al*. J. Quant. Spectrosc. Rad. Transf. 99, 658 (2006)
PARADISIO M. Pénicaud, J. Phys. Cond. Matt. 21, 095409 (2009)

Variational Average Atom – Piron, Blenski, & Cichocki



Does the truncated cluster expansion retain variational property?
Ion radial distribution averaged away? (Ion-Ion interactions are gone.)

- **Single nucleus, charge *Z*, at origin.**
- **Charge neutrality inside sphere determines *R*.**

$$R=(3/4\pi n_i)^{1/3}$$

- **Ion distribution** $G(r)\approx\theta(r-R)$
- **Free energy expansion w/r reference jelium n_0 terminated at first-order**

$$\mathcal{F}[n\,|\,n_0,n_I,\beta]=\mathcal{F}_0[n_0,n_I,\beta]+\Delta\mathcal{F}_1[n\,|\,n_0,n_I,\beta]$$

- **Use this as a variational expression with n_0 to be determined self-consistently.**
- $\Delta\mathcal{F}_1$ **is shift of free energy of ion with respect to jelium – akin to an INFERNO-like shift**
- **Finite-T DFT (with Dirac-Kohn-Sham) for** $\Delta\mathcal{F}_1$
- **XC=LDA, finite-T Perrot 1979, Ichimaru *at al.* 1987**
- **Virial pressure**

R. Piron, T. Blenski, and B. Cichocki, J. Phys. A Math. Theor. 42, 214059 (2009)
R. Piron and T. Blenski, Phys. Rev. E 83, 026403 (2011)

Variational Average Atom with Radial Ion-Ion Correlations

- **Single nucleus, charge *Z*, at origin**
- **Ion distribution outside is included in spherically averaged sense.**
- **Ion distribution constructed consistently with nucleus-centered problem**
- **Uses DFT for ions and electrons**
- **Truncates "excess" free energy (non-ideal contribution) at second-order in functional Taylor expansion around reference densities -**

$$\Delta\mathcal{F}^{exc}[n_e,n_I]=\mathcal{F}^{exc}[n_e,n_I]-\mathcal{F}^{exc}[n_e^0,n_I^0]$$

$$=\mu_e^{exc}\int d\mathbf{r}\Delta n_e(\mathbf{r})+\mu_I^{exc}\int d\mathbf{r}\Delta n_I(\mathbf{r})+\int d\mathbf{r}_1 d\mathbf{r}_2\Delta n_e(\mathbf{r}_1)\Delta n_I(\mathbf{r}_2)\left.\frac{\delta^2\mathcal{F}^{exc}}{\delta n_e(\mathbf{r}_1)\delta n_I(\mathbf{r}_2)}\right|_{V_I^{ext}=V_e^{ext}=0}$$

$$+\frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\Delta n_I(\mathbf{r}_1)\Delta n_I(\mathbf{r}_2)\left.\frac{\delta^2\mathcal{F}^{exc}}{\delta n_I(\mathbf{r}_1)\delta n_I(\mathbf{r}_2)}\right|_{V_I^{ext}=V_e^{ext}=0}+\frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\Delta n_e(\mathbf{r}_1)\Delta n_e(\mathbf{r}_2)\left.\frac{\delta^2\mathcal{F}^{exc}}{\delta n_e(\mathbf{r}_1)\delta n_e(\mathbf{r}_2)}\right|_{V_I^{ext}=V_e^{ext}=0}$$

$$+\cdots$$

- **Functional derivatives are closely related to "direct correlation functions"**
- **Satisfy quantum Ornstein-Zernike equations.**

Talk by D. Saumon

C.E. Starrett and D. Saumon, Phys. Rev. E 85, 026403 (2012)

Calibration of Approximate Functionals? PIMC

Factorization to paths

$$\rho\left(\{\mathbf{r}\},\{\mathbf{r}'\};\beta\right)=\sum_i \Psi_i^*\left(\{\mathbf{r}\}\right)\exp(-\beta E_i)\Psi_i\left(\{\mathbf{r}'\}\right)$$

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

$$\exp(-\beta\hat{\mathcal{H}})=\left\{\exp[-(\beta/M)\hat{\mathcal{H}}]\right\}^M := \left\{\exp(-\tau\hat{\mathcal{H}})\right\}^M$$

$$\rho\left(\{\mathbf{r}\}_0,\{\mathbf{r}\}_M;\beta\right)=\int d\{\mathbf{r}\}_1\cdots d\{\mathbf{r}\}_{M-1}\,\rho\left(\{\mathbf{r}\}_0,\{\mathbf{r}\}_1;\tau\right)\cdots\rho\left(\{\mathbf{r}\}_{M-1},\{\mathbf{r}\}_M;\tau\right)$$

Despite the fact that KE and PE operators don't commute

$$\exp(-\beta\hat{\mathcal{H}})=\lim_{M\to\infty}\left\{\exp[-(\beta/M)\hat{\mathcal{T}}-(\beta/M)\hat{V}]\right\}^M$$

This allows separation of KE and PE contributions

$$\rho\left(\{\mathbf{r}\}_0,\{\mathbf{r}\}_M;\beta\right)=\frac{1}{(4\pi\Lambda_e\tau)^{(3N_eM/2)}}\int d\{\mathbf{r}\}_1\cdots d\{\mathbf{r}\}_{M-1}\exp\left[-\sum_1^M\frac{(\{\mathbf{r}\}_{M-1}-\{\mathbf{r}\}_M)^2}{4\Lambda_e\tau}+\tau V(\{\mathbf{r}\}_M)\right]$$

which has a non-negative integrand – good for MC sampling. Fermion anti-symmetry still to be imposed. D. Ceperley's talk.

"Computational Methods for Correlated Systems, Lecture 3"
http://www.phys.ufl.edu/courses/phy7097-cmt/fall08/lectures/index.html
"Path Integral Monte Carlo" B. Bernu and D.M. Ceperley
http://www2.fz-juelich.de/nic-series/volume10/volume10.html

ftDFT in practice today

- **Typically one of two flavors**
  - **BOMD with a code such as VASP and $\mathcal{F}_{xc}[n(T), T] \approx E_{xc}[n(T)]$**
  - **Some form of Thomas-Fermi + von Weizsäcker for KE (discussion below about orbital-free schemes)**

Talks by Ronald Redmer, Joel Kress, Flavien Lambert, (others ?)

Q: Is a ground state functional with implicit *T*-dependence good enough?

Talk by Travis Sjostrom

- **Many-body transport coefficients calculated with Kohn-Sham inputs.**

Example: Kubo-Greenwood electrical conductivity:

$$\sigma(\omega) = \sum_{\mathbf{k}\in \mathbf{BZ}} w_{\mathbf{k}} \sigma_{\mathbf{k}}(\omega)$$

$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi}{3V\omega} \sum_{i,j} \sum_{\mu} \left| \left\langle \varphi_{i\mathbf{k}} \middle| \nabla_{\mu} \middle| \varphi_{j\mathbf{k}} \right\rangle \right|^2 \left(f_{i\mathbf{k}} - f_{j\mathbf{k}} \right) \delta\left(\varepsilon_{i\mathbf{k}} - \varepsilon_{j\mathbf{k}} - \omega \right)$$

Remark: In principle, this is a misuse of the KS orbitals and eigenvalues.

Q: How good (bad) an approximation is it to do that?

Q: What can be done to characterize (and, one hopes, bound) the errors from doing that?

Quantum Stat. Mech. for WDM – Miscellaneous Remarks

- **Discussion of coupled-cluster methods omitted from $T=0$ K QM survey for brevity. For small molecules, these generally are accepted as the "gold standard" for calibration and validation of other methods (in some aspects better than experiment).**
- **Omitted quantum statistical potentials, wave packet MD, PIMD, DFT embedding, QM Green's fns, hybrid functionals, range separation, time-dep. DFT, …**
- **The literature for quantum stat. mech. relevant to WDM is scattered in maddeningly many disparate journals: Phys. Rev. A, B, E; Phys. Rev. Lett.; J. Chem. Phys.; J. Phys. Cond. Matt.; J. Phys. A; J. Phys. Chem.; J Chem. Th. Computation; Phys. Plasmas; High En. Dens. Phys.; Contrib. Plasma Phys.; J. Quant. Spectr. Rad. Transf.; Comput. Phys. Commun.; Phys. Chem. Liq.; J. Non-Cryst. Solids; Theoret. Chem. Accounts; … etc.**
- **Plasma community makes assumptions about the readership which are at odds with the diversity of backgrounds from which folks come to WDM.**
- **Conversely, the jargon of many-body and cond. matter physics can be difficult and the jargon of quantum chemistry is far more so.**
- **Despite convenient language, BOMD with quantum stat. mech. electronic forces is not "quantum MD".**

Orbital-free DFT – Aspects of Approximate Functional Development

OFDFT MOTIVATION -

- **A personal fascination**
- **A potentially enormous boost to WDM simulations**

☞ **The K-S decomposition is valuable: it provides a one-body system that gives the physical density and free energy.**

☞ **But the K-S orbital structure is**

- **expensive computationally**
- **not essential conceptually**

Constraint-based Orbital-free finite-temperature DFT (“of-ftDFT”)

of-ftDFT is back to basics:

$$\mathcal{T}_s[n,T] = \int d\mathbf{r}\; t_S[n(\mathbf{r}),T]$$

$$\mathcal{S}_s[n,T] = k_B \int d\mathbf{r}\; s_S[n(\mathbf{r}),T]$$

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

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

exact at *T= 0* K and finite T [PRB 84, 125118 (2011)]

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

Then given $\mathcal{F}_{\mathrm{xc}}$, the of-ftDT Euler equation is

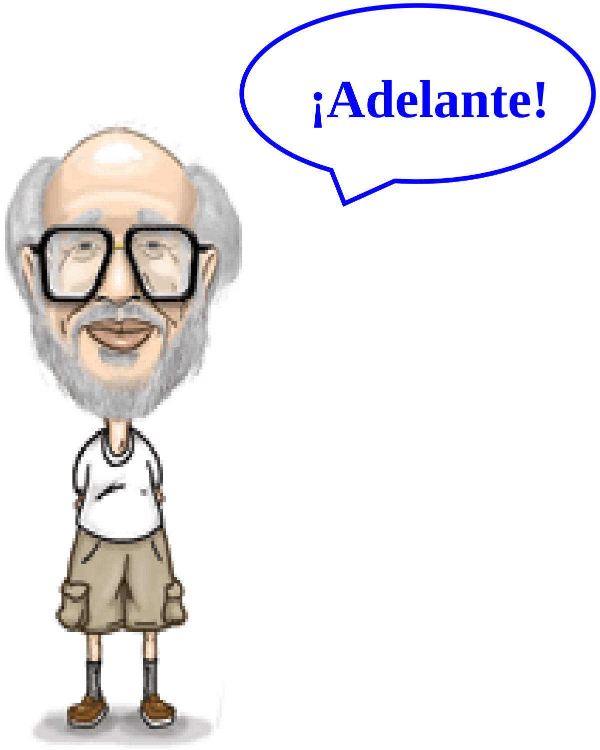
$$\left(-\frac{1}{2}\nabla^2 + v_{KS}(\mathrm{r}) + v_\theta(\mathrm{r})\right)\sqrt{n(\mathrm{r})} = \mu\sqrt{n(\mathrm{r})}$$

$$v_\theta(\mathrm{r}) = \delta(\mathcal{T}_\theta - T\mathcal{S}_s)/\delta n \;, \quad \lim_{T\to 0} v_\theta \geq 0 \quad \forall\ \mathrm{r}$$

Adventures in Constraint-based functional development

- **<u>Four</u> challenges –**
    - **a) Non-interacting $\mathcal{F}_s$ has two contributions: KE and entropy**
    - **b) $\mathcal{F}_{xc}$ has two contributions: X, C**
- **Task – design functionals which respect as many known results (limits, bounds, asymptotics, etc.) as possible.**
- **Remarks:**
    - **a) Frequent criticism of *T=0* K KS-DFT is “there is no systematic way to improve the XC functionals”. A more accurate remark is that there is no mechanical recipe to add complexity to XC functionals.**
    - **b) Added complexity is not a guarantee of improved accuracy**
    - **c) There is a horrendous amount of empiricism, fiddling, and combining of bits and pieces of functionals to achieve “successful” error cancellation (mostly in quantum chemistry). Most of this can be ignored beneficially.**
    - **d) But some empirical functionals are useful for showing how much can be achieved with a given level of complexity or refinement.**

Sam's Excellent Adventures in Functional Design



Credit: Bobby Scurlock

T= 0 K X , Lieb-Oxford Bound, and Generalized Gradient Approximations

$$E_{xc} \geq \lambda_{LO} E_x^{LDA} \; ; \quad \lambda_{LO} = 2.275 \quad (\lambda_{LO,CH} = 2.2149)$$

$$E_x^{LDA} = c_x \int d\mathbf{r}\, n^{4/3}(\mathbf{r}) \, , \quad c_x := -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Constraint on construction of XC functionals

E. Lieb and S. Oxford, Int. J. Quantum Chem. 19, 427 (1981); J.P. Perdew in "Electronic Struct. Of Solids '91", 11 (1991); G. Chan and N. Handy, Phys. Rev. A 59, 3075 (1999)

Generalized Gradient Approximation for X

$$E_x^{GGA}[n] = c_x \int n^{4/3}(\mathbf{r}) F_{xGGA}(s(\mathbf{r})) d\mathbf{r}$$

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

Satisfaction of the L-O bound for all possible spin densities n_σ(r), and all inhomogeneity values *s*(r) imposed as a sufficient condition -

$$F_{x,GGA}[n,s] \leq \frac{\lambda_{LO}}{2^{1/3}} \approx 1.804$$

Vela-Medel-Trickey X Enhancement Factor (VMT) -

- $s \rightarrow 0 : F_x^{VMT} \rightarrow 1$ **(homogeneous electron gas)**
- **Lieb-Oxford bound :** $F_x^{VMT} \leq 1.804$
- **Large** s **limit** $\rightarrow$ **homogeneous electron gas**

$$F_x^{VMT}(s) \quad = \quad 1 \quad + \quad \frac{\mu\, s^2\, e^{-\alpha\, s^2}}{1 + \mu\, s^2}$$

$$\text{where} \quad \mu = \frac{10}{81} \quad \Rightarrow \quad \text{GEA (PBEsol)} \quad \text{or } \mu = 0.21951 \text{ (PBE)}$$

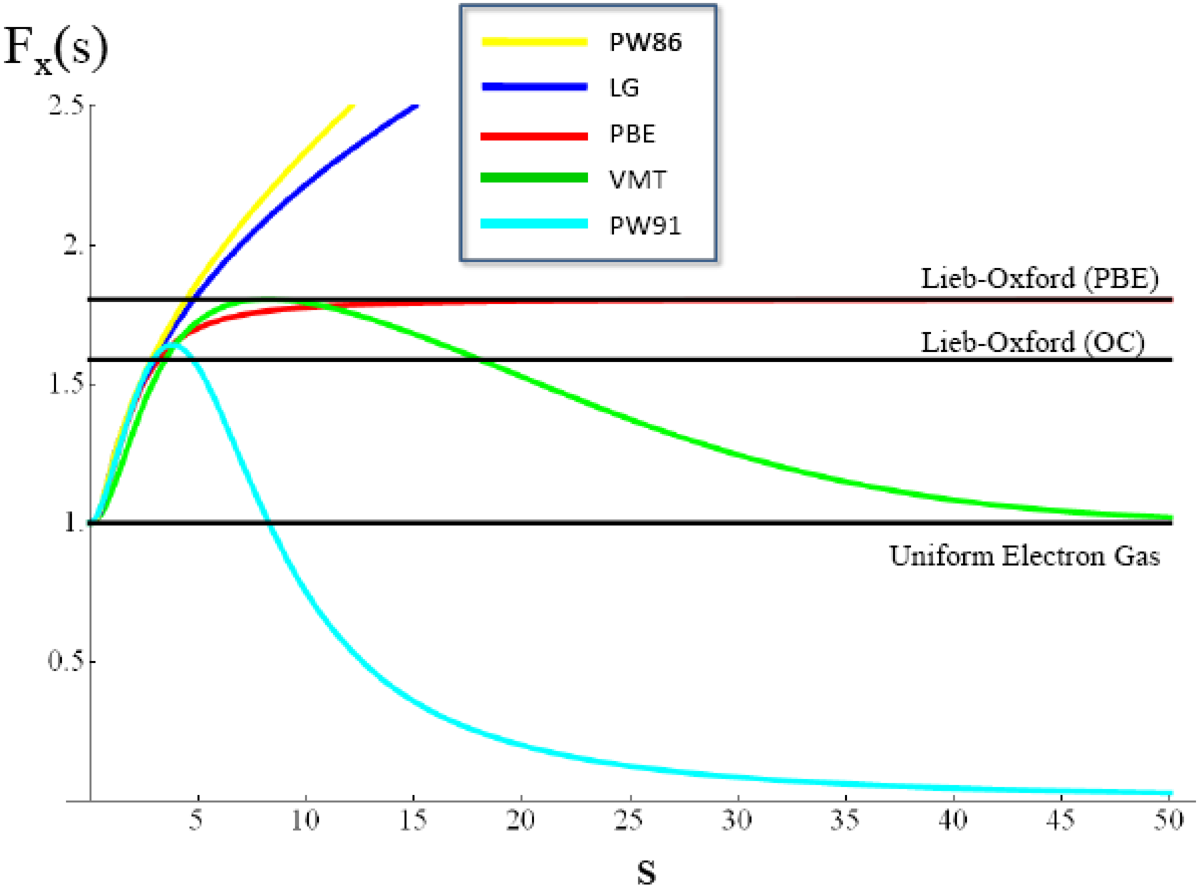
$$\alpha \ni F_x^{VMT}(s_{MAX}) = \lambda_{LO} / 2^{1/3}$$

$$s_{MAX} := \sqrt{\frac{81}{20}\left(\sqrt{\frac{40/81 + \alpha}{\alpha}} - 1\right)}$$

Reminder: $$F_x^{PBE} := 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}$$

J. Chem. Phys. 130, 244103 (2009)

Comparison of X Enhancement Factors -



Only PW91 X satisfies the large-s constraint

$$\lim_{s\to\infty} s^{1/2} F_{XC} < \infty$$

M. Levy & J.P. Perdew, Phys. Rev. B 48, 11638 (1993)

VT{84} Exchange

VMT **recovers HEG behavior for large-s while staying below the LO bound for all but one value of *s***

$$F_X^{VMT}(s) = 1 + \frac{\mu s^2 e^{-\alpha s^2}}{1+\mu s^2}$$

VT{mn} **adds satisfaction of the large-*s* constraint**

$$F_X^{VT\{mn\}}(s) = F_X^{VMT}(s) + \left(1-e^{-\alpha s^{m/2}}\right)\left(s^{-n/2}-1\right)$$

$$= 1 + \frac{\mu s^2 e^{-\alpha s^2}}{1+\mu s^2} + \left(1-e^{-\alpha s^{m/2}}\right)\left(s^{-n/2}-1\right)$$

FUNCTIONAL DESIGN: m **and *n* are fixed by:**

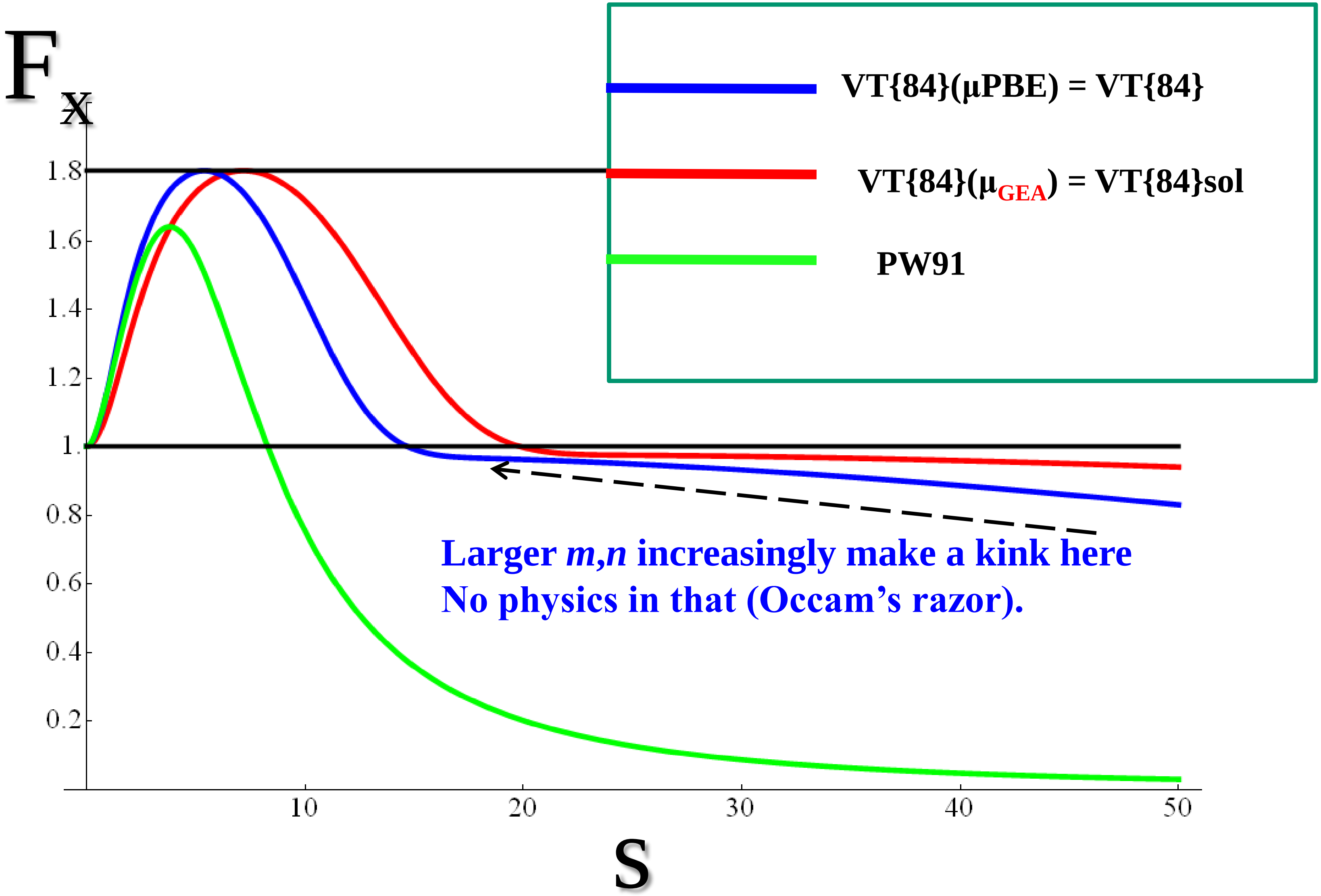
- ***m, n*** **must be integers.**
- **The leading term in the small-*s* expansion of F_x must be quadratic.**
- **Rotational invariance ⇒ only even powers of *s* are allowed.**
- **Limit $s \to 0$ must $= 1$ to recover HEG behavior.**

$$\Rightarrow m > n; \quad m/2 \text{ and } (m-n)/2 \text{ are even}$$

***m,n* = 8,4: α_{PBE} = 0.000069, α_{GEA} = 0.000023**

J. Chem. Phys. 136, 144115 (2012)

Why 8,4? Design Choices



Larger *m*,*n* increasingly make a kink here
No physics in that (Occam's razor).

VT{84} and VMT: Molecular Tests

Typical Test Sets in this specialty: Raghavachari, Curtiss, Perdew, Scuseria, Truhlar, Hobza, Cheeseman

- **G1 for atomization energies (fixed geometries).**
- **G3 for standard heats of formation at 298 K (geometry optimizations + harmonic analysis). Only example presented here.**
- **Ionization potentials, electron and proton affinities with optimized geometries.**
- **Weak interactions.**
- **Hydrogen and non-hydrogen transfer barrier heights (fixed geometries).**
- **Transition metals**
- **Chemical shifts**
- **VT{mn} and VMT implemented in development versions of deMon2k and NWChem.**

VT{84} and VMT: Molecular Tests

G3 Data Set: Mean Absolute Errors for Standard heats of formation at 298 K / kcal-mol^{-1} (223 molecules) TPSS is a “meta-GGA”, LYP is a correlation functional. 1 kcal/mol = 0.043 eV/atom

VT{84} is 53% better than PBE-PBE and 42% with LYP (PBE-LYP vs. VT{84} –LYP) using a TZVPP basis set

		TPSS	PBEsol	PBE	VMT	VT84	VMTsol	VT84sol
PBE-C except TPSS	DZVP	8.22	55.32	20.38	10.87	10.20	48.98	48.58
	def2-TZVPP	5.40	59.63	21.92	11.00	10.42	53.01	52.58
LYP-C except TPSS	DZVP	8.22	39.55	11.89	7.79	8.14	33.43	33.05
	def2-TZVPP	5.40	43.53	13.04	7.48	7.63	36.97	36.55

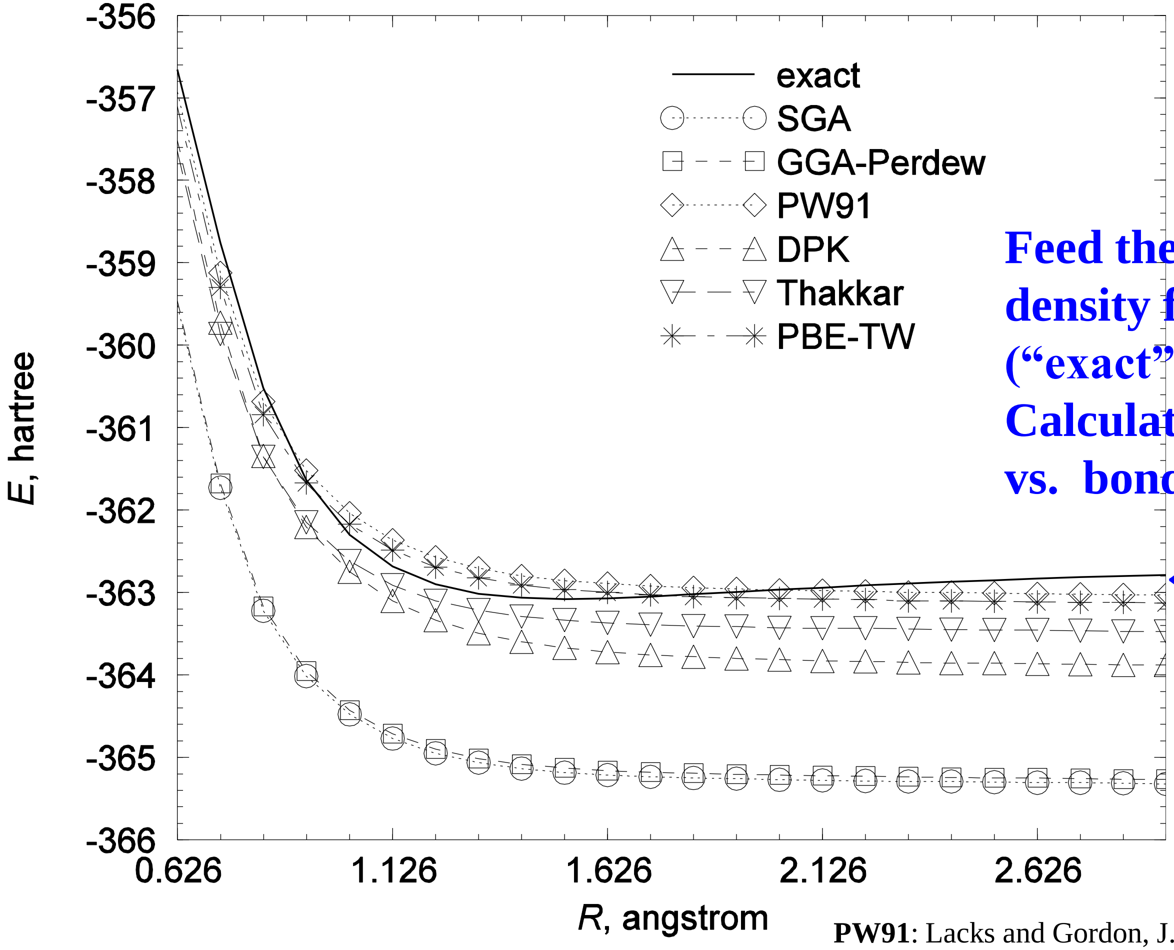
J. Chem. Phys. 136, 144115 (2012)

But that's only XC

Those benchmark calculations were pure Kohn-Sham -

- ☞ **KS KE without orbitals?**
- ☞ **KS entropy without orbitals?**

OF-DFT at T=0 K: Test of Existing Single-point (GGA) KE functionals



← **KS**

Feed the OF-KE functionals the density from the KS calculation ("exact" for these purposes). Calculate new total energy vs. bond length for SiO stretch.

All six T_s approximations fail to bind! V_θ violates positivity.

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

PW91: Lacks and Gordon, J.Chem. Phys. 100, 4446 (1994)
PBE-TW: Tran and Wesolowski, Internat. J. Quantum Chem. 89, 441 (2002) [
GGA-Perdew: Perdew, Phys. Lett. A 165, 79 (1992)
DPK: DePristo and Kress, Phys. Rev. A 35, 438 (1987)
Thakkar: Thakkar, Phys. Rev. A 46, 6920 (1992)
SGA: Second order Gradient Approx. $\mathcal{T}_S = \mathcal{T}_{TF} + (1/9)\ \mathcal{T}_W$

OF-KE at T=0 K: 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.**

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

"Conjoint" - $F_t \propto F_x$
***N*=2 is typical PBE form; also used by Tran & Weslowski**
***N*=3 is the form used by Adamo & Barone** [J. Chem. Phys. **116**, 5933 (2002)]
***N*=4 highest tried**

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

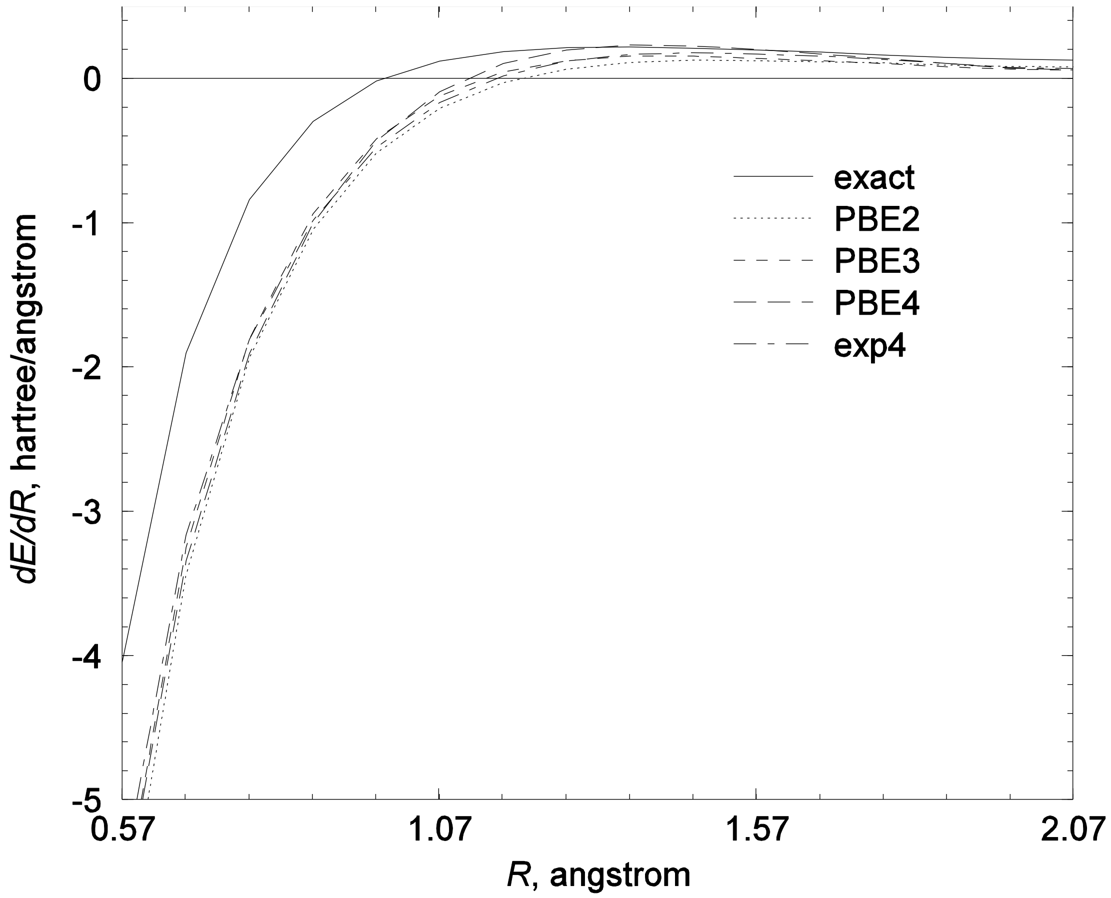
- **Constrain parameters to** $v_\theta \geq 0$

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-KE at T=0 K – Test of Modified Conjoint, Positive-definite Functionals

Single bond stretch gradient for H_2O (negative of force).

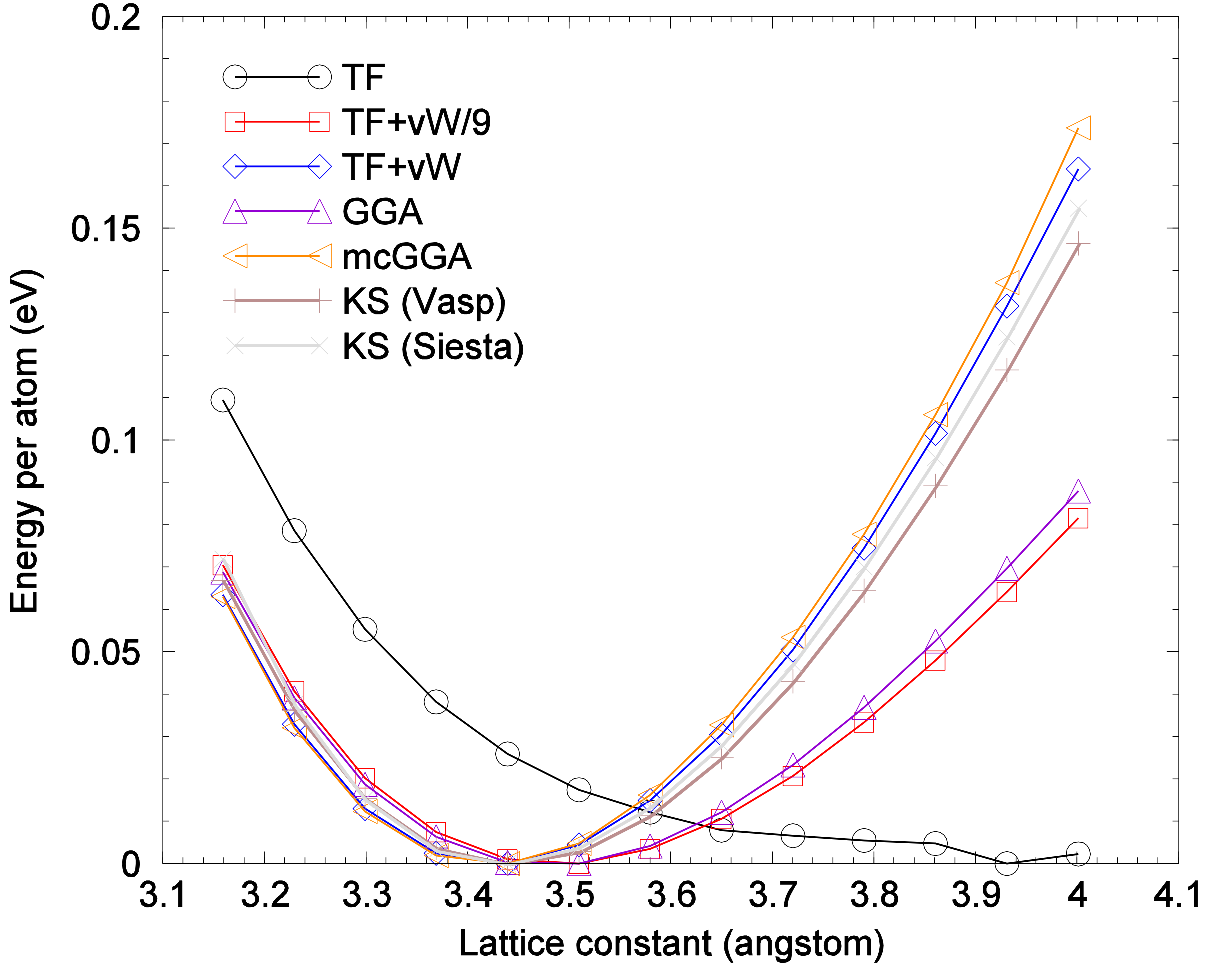
OF-KE parameters from 3-member training set (SiO, H_4SiO_4, and $H_6Si_2O_7$) except PBE2.
NO information about H_2O in the set.



All our functionals give too large an equilibrium bond length from input KS density.
PROBLEM: mcGGA Pauli potential v_θ singularities at nuclei. TOO positive!

Phys. Rev. B 80, 245120 (2009).

Are mcGGA Positive Singularities Fatal?



No.

Bcc Li lattice constant. mcGGA is our PBE-2, parameterized to SiO , implemented in modified PROFESS code. GGA=Tran & Wesołowski

New of-ftDFT functionals – non-interacting part

New Finite-*T* generalized gradient approximation via new variables.

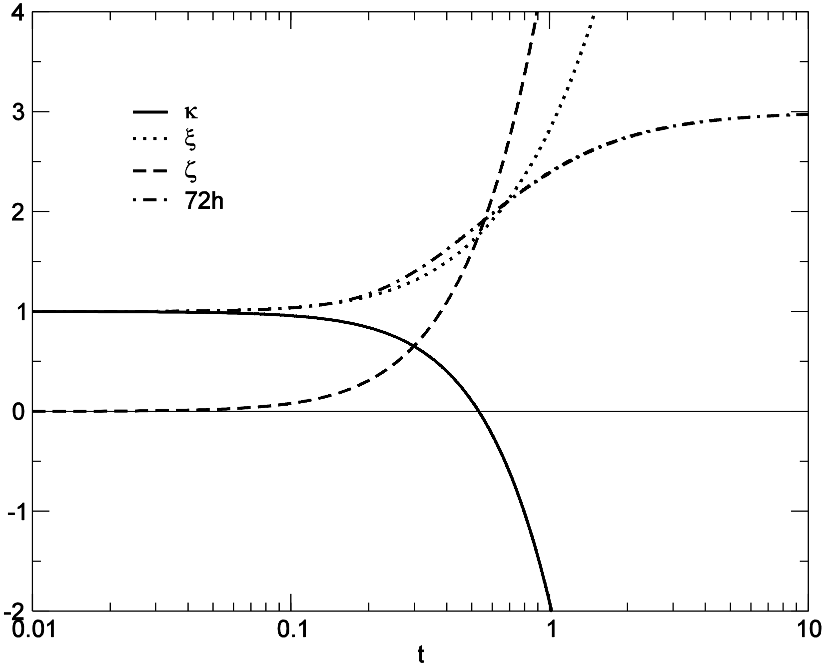
$$\mathcal{F}_s^{ftGGA}[n] = \int d\mathbf{r}\left[\tau_0^{\mathrm{TF}}(n)\xi(t)F_\tau(s_\tau)\right] - \int d\mathbf{r}\left[\tau_0^{\mathrm{TF}}(n)\zeta(t)F_\sigma(s_\sigma)\right]$$

$$s_\tau(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{\tilde{h}(t) - \mathrm{t}\,\mathrm{d}\tilde{h}(t)/\mathrm{dt}}{\xi(t)}}$$

$$s_\sigma(n,\nabla n,\mathrm{T}) := s(n,\nabla n)\sqrt{\frac{\mathrm{t}\,\mathrm{d}\tilde{h}(t)/\mathrm{dt}}{\zeta(t)}}$$

$$t = T/T_F$$

Form of new variables motivated by 2nd order gradient expansion.



$\tilde{h}$ from Perrot's (1979) analytic fit
Beware one obviously wrong coefficient (exponent) in that fit.

Details: Valentin Karasiev's Poster

New of-ftDFT functionals – non-interacting part

First try (known to violate some constraints; satisfies an approximate symmetry)

$$F_\tau^{\mathrm{KST2}}(s_\tau) := 1 + \frac{C_1 s_\tau^2}{1 + a_1 s_\tau^2}$$

$$F_\sigma^{\mathrm{KST2}}(s_\sigma) := 1 - \frac{C_1 s_\sigma^2}{1 + a_1 s_\sigma^2}$$

$\mathrm{C}_1 = 2.03087$, $\mathrm{a}_1 = 0.29424$

mcGGA "PBE2" with new finite-*T* inhomogeneity variables

Parameters fitted at *T = 0* K to *small* training set

Phys. Rev. B 80, 245120 (2009)

ftGGA based on Tran-Wesolwski *T = 0* K ofKE GGA

Int. J. Quantum Chem. 89, 441 (2002)

$\mathrm{C}_1^{TW} = 0.2319$, $\mathrm{a}_1^{TW} = 0.2748$

Details: Valentin Karasiev's Poster

Codes and Pseudo-potentials

ofDFT - PROFESS (modified for single-point functionals)

Comput. Phys. Commun. 181, 2208 (2010); *ibid.* 179, 839 (2008))

64 atom supercell

KS-pseudopot – AbInit;

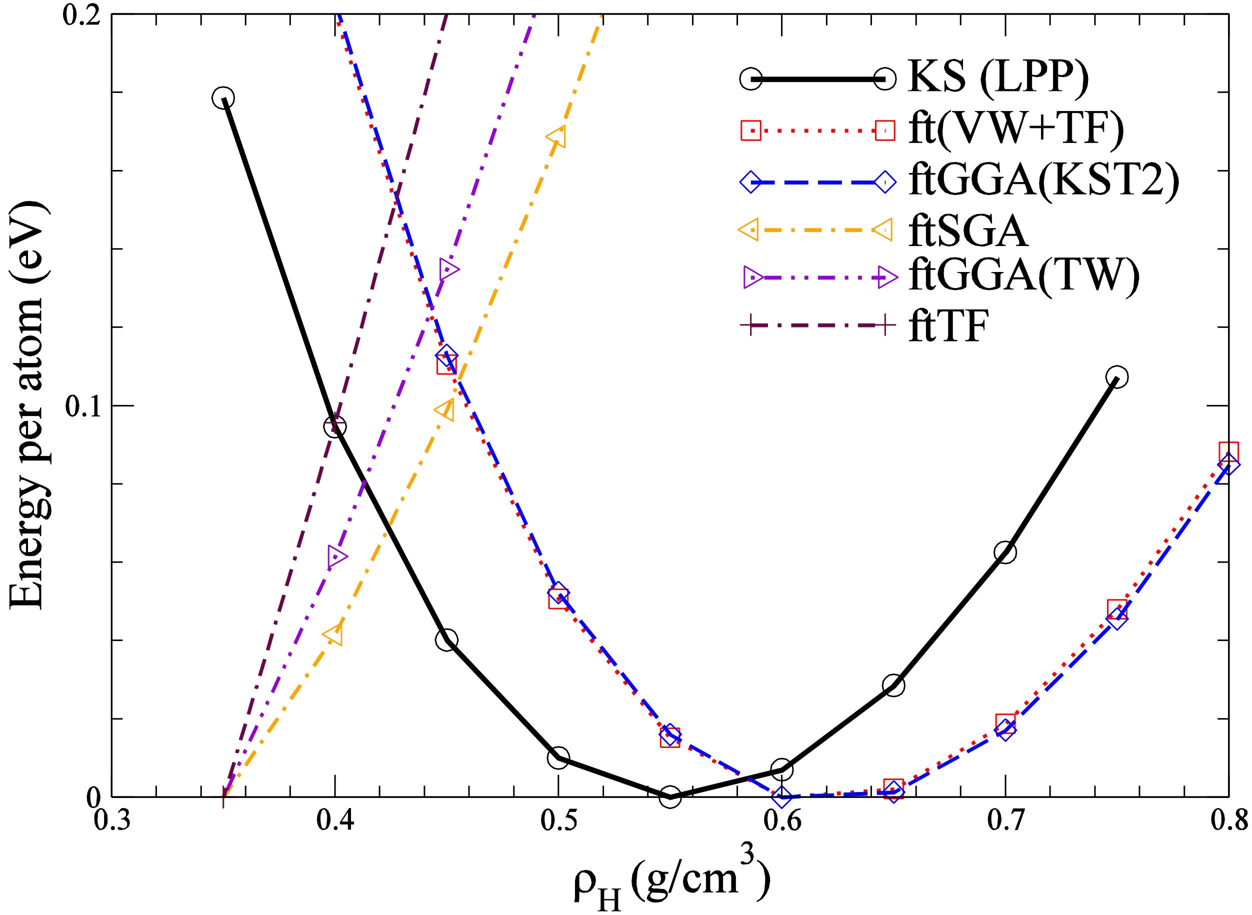
Comput. Phys. Commun. 180, 2582 (2009)

8-atom cell, 13 x 13 x 13 k-mesh

Pseudo-potential –
Heine-Abarenkov
Parameters adjusted to match PAW ground-state optimized sc-H lattice constant (a = 1.447 Å) with PZ LDA in AbInit.

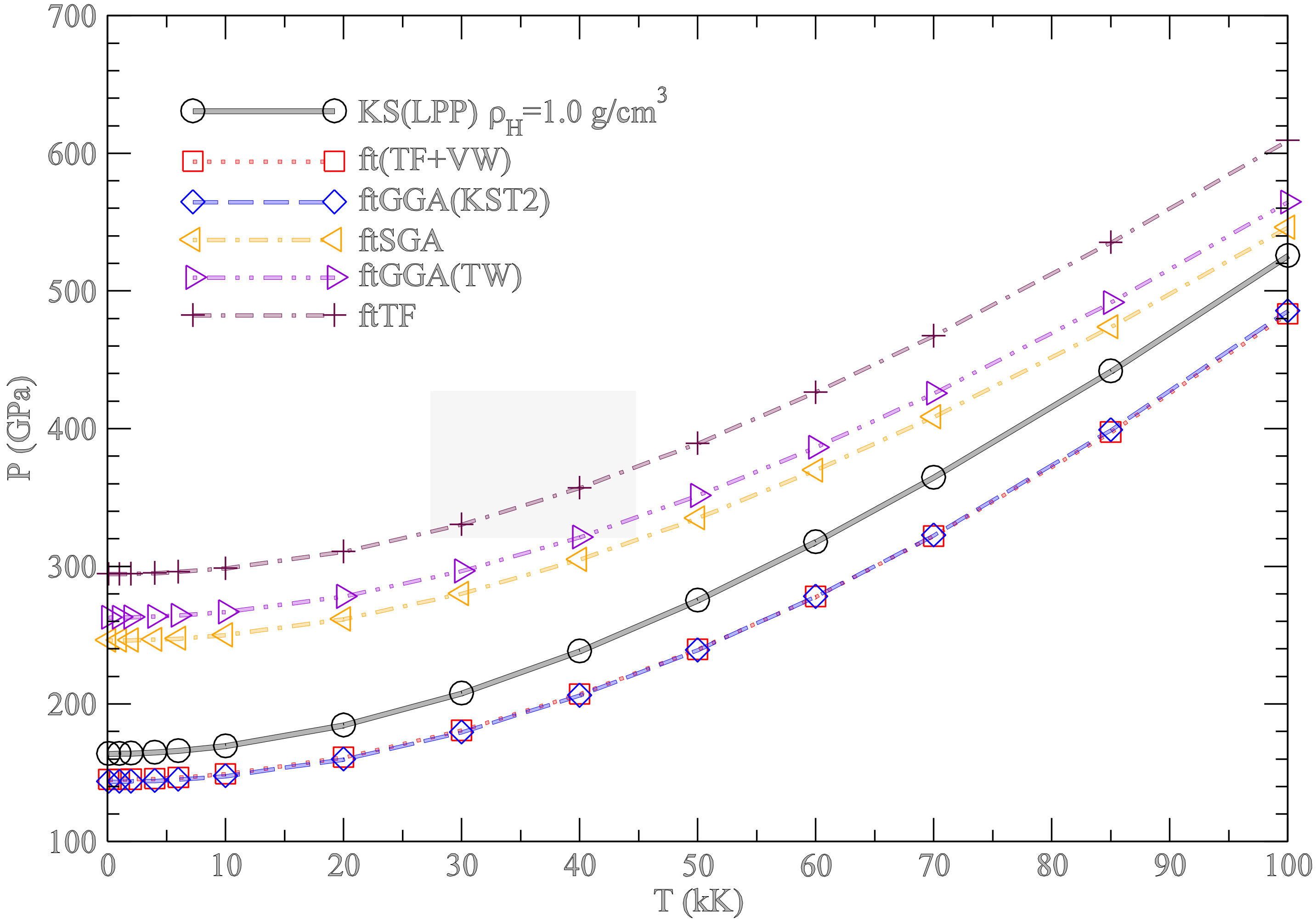
Details: Valentin Karasiev's Poster

Structural Optimization Comparison



Energy per atom vs. material density for sc-H at electronic temperature T_e=100 K (T_{ion}=0 K) for KS and OF-DFT calculations (both with PZ LDA XC functional and Heine-Abarenkov local pseudo-pot. *Nota bene*: VW+TF is full VW, ftSGA is VW/9.

sc Hydrogen



P **vs.** ***T*** **for five orbital-free functionals and tKS. Simple cubic H, ρ=1.0 g/cm^3 (compression ≈ 1.8) All with LDA** ***E_{xc}*****. Includes ion-ion contribution.**

UNIVERSITY of FLORIDA

scH data for tKS vs of-tDFT

T (Kelvin)	P(Tpa) tKS-LDA	P(Tpa) SGA = tTF + tvW/9	P(Tpa) tTF	P(Tpa) tGGA KST2	P(Tpa) tGGA TW
100	0.1640	0.2463	0.2945	0.1438	0.2631
1000	0.1641	0.2463	0.2946	0.1438	0.2631
10,000	0.1696	0.2502	0.2986	0.1478	0.2669
50,000	0.2754	0.3351	0.3893	0.2393	0.3515
100,000	0.5258	0.5463	0.6094	0.4856	0.5646

ρ=1.0 g/cm^3 (compression ≈ 1.8) All with PZ E_{xc} LDA as approximate F_{xc} .
Includes ion-ion contribution.
Red headings denote failure to give stable ground state.

Finite-T Exchange-correlation free energy

$$\mathcal{F}_{xc} = \int d\mathbf{r}\; n(\mathbf{r})\; \mathrm{f}_{xc}[n(\mathbf{r}), T]$$

See Travis Sjostrom's talk for comparison of three *T*-dependent C functionals.

References – OF-KE and thermal DFT

- “Generalized Gradient Approximation Non-interacting Free Energy Functionals for Orbital-free Density Functional Calculations”, V.V. Karasiev, T. Sjostrom, and S.B. Trickey, in preparation
- “Issues and Challenges in Orbital-free Density Functional Calculations”, V.V. Karasiev and S.B. Trickey, Comput. Phys. Commun. [accepted]
- “Comparison of Density Functional Approximations and the Finite-temperature Hartree-Fock Approximation for Warm Dense Lithium”, V.V. Karasiev, T. Sjostrom, and S.B. Trickey, in preparation
- “Finite Temperature Scaling, Bounds, and Inequalities for the Noninteracting Density Functionals”, J.W. Dufty and S. B. Trickey, Phys. Rev. B 84, 125118 (2011)
- “Positivity Constraints and Information-theoretical Kinetic Energy Functionals”, S.B. Trickey, V.V. Karasiev, and A. Vela, Phys. Rev. B 84, 075146 [7 pp] (2011).
- “Temperature-Dependent Behavior of Confined Many-electron Systems in the Hartree-Fock Approximation”, T. Sjostrom, F.E. Harris, and S.B. Trickey, Phys. Rev. B 85, 045125 (2012)
- “Constraint-based, Single-point Approximate Kinetic Energy Functionals”, V.V. Karasiev, R.S. Jones, S.B. Trickey, and F.E. Harris, Phys. Rev. B 80, 245120 (2009)
- “Conditions on the Kohn-Sham Kinetic Energy and Associated Density”, S.B. Trickey, V.V. Karasiev, and R.S. Jones, Internat. J. Quantum Chem.109, 2943 (2009)
- “Recent Advances in Developing Orbital-free Kinetic Energy Functionals”, V.V. Karasiev, R.S. Jones, S.B. Trickey, and F.E. Harris, in *New Developments in Quantum Chemistry*, J.L. Paz and A.J. Hernández eds. [Research Signposts, 2009] 25-54
- “Born-Oppenheimer Interatomic Forces from Simple, Local Kinetic Energy Density Functionals”, V.V. Karasiev, S.B. Trickey, and F.E. Harris, J. Computer-Aided Mat. Design, 13, 111-129 (2006)

http://www.qtp.ufl.edu/ofdft