UF UNIVERSITY of FLORIDA

# Temperature-Dependent Behavior of Confined Many-electron Systems in the Hartree-Fock Approximation


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*Collaborators* (*Orbital-free KE & FE functionals*):

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**Vivek Kapila (Univ. Florida)**

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## *Background and Challenge*

- ❖ **Motivation: Simulation of the Physics of Warm Dense Matter**
- ❖ **Reminder: Finite-temperature, Orbital-free Free Energy Density Functionals**
  - **Objectives:**
    **Practical - drive molecular dynamics**
    **Conceptual – realize fundamental content of DFT**
  - **Kohn-Sham kinetic energy contribution**
  - **Kohn-Sham entropy contribution**
  - **Exchange-correlation free energy**
  - **Implicit T dependence of ground-state functionals**
- ❖ **Challenge: Scarcity of data for finite-temperature, inhomogeneous, many-electron systems.**
- ❖ **Response: Thermal Hartree-Fock calculations on confined, many- electron systems ( = this talk).**

## *Thermal Hartree-Fock Theory*

**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 (Hartree atomic units) are:**

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

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

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

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

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

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

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

**The trace "*N,SD*" is over all N-electron Slater determinants.**

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

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

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

## *Confined System*

- **The model problem is a hard-walled rectangular parallelepiped containing a few (1-8) 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* → ∞).**
- **Temperature range: 0 ≤ *T* ≤ 300,000 K.**

**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.**

$$g^n_{box}(x) := \begin{cases} a_0\left[g^n(x) - g^n(0)\right] & 0 \le x \le x_c \\ a_L\left[g^n(x) - g^n(L_x)\right] & x_c \le x \le L_x \end{cases}$$

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

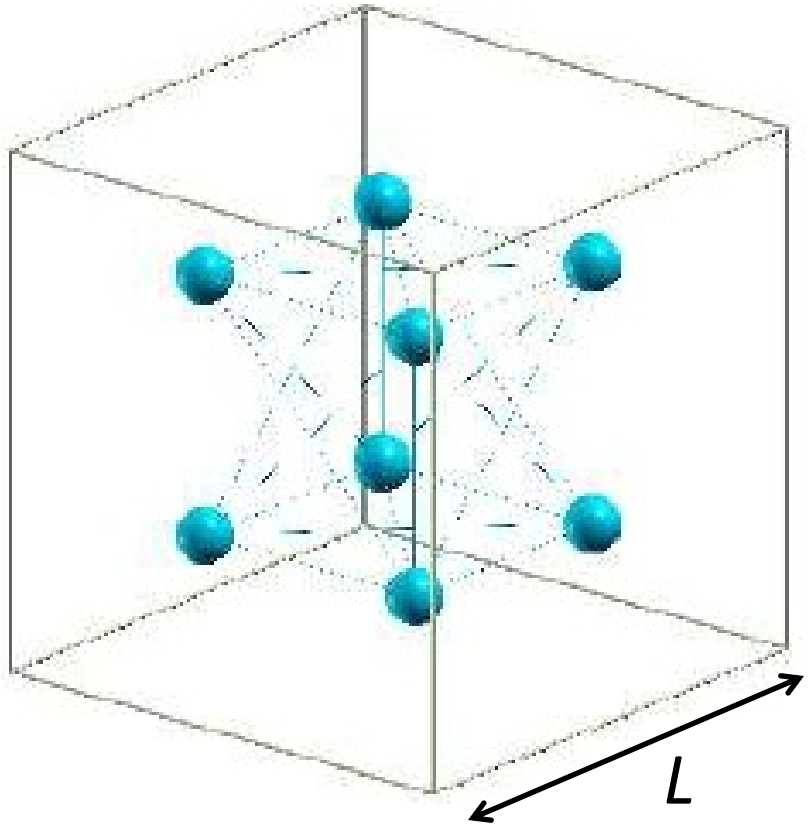
$x_c$ is nucleus position.

**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.**

- **Test cases completed – H and H2 at free limit and compressed.**

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



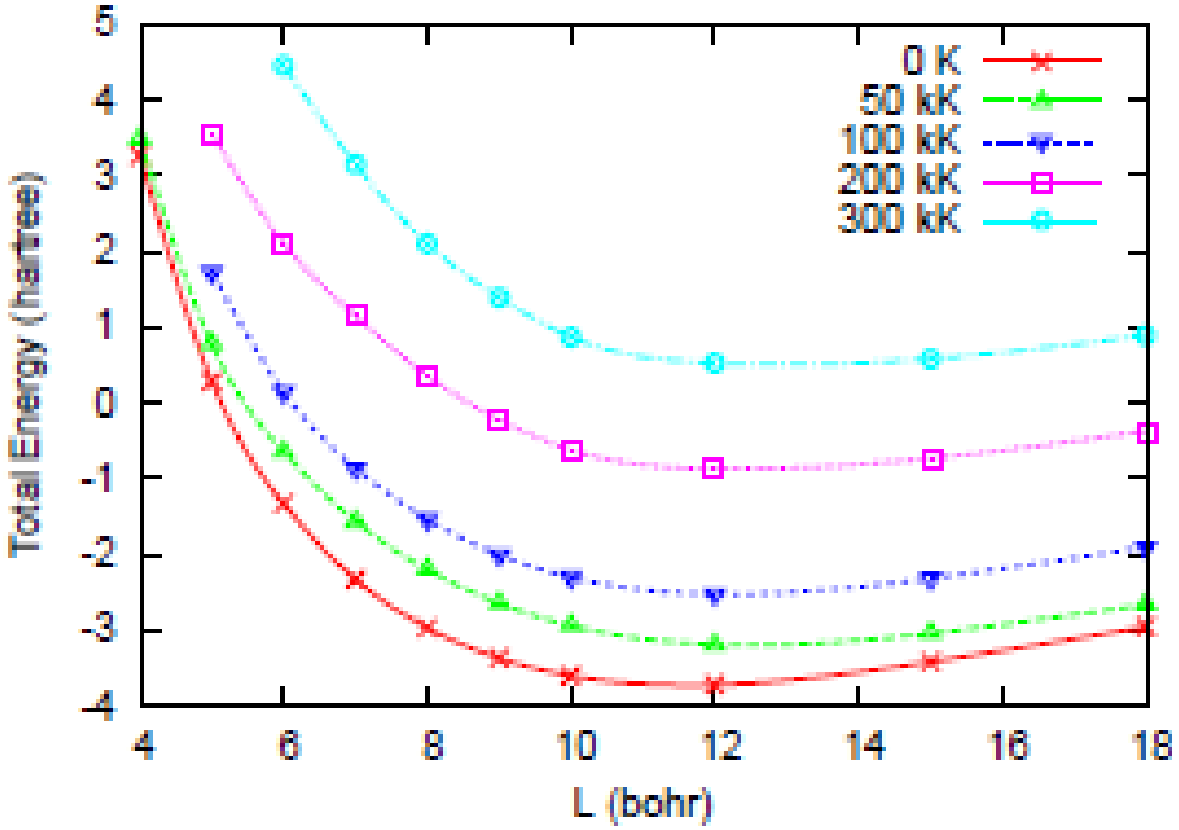

**Distance:**

Atom to near walls = ***L*/4**

Atom to nearest atom = ***L*/2**

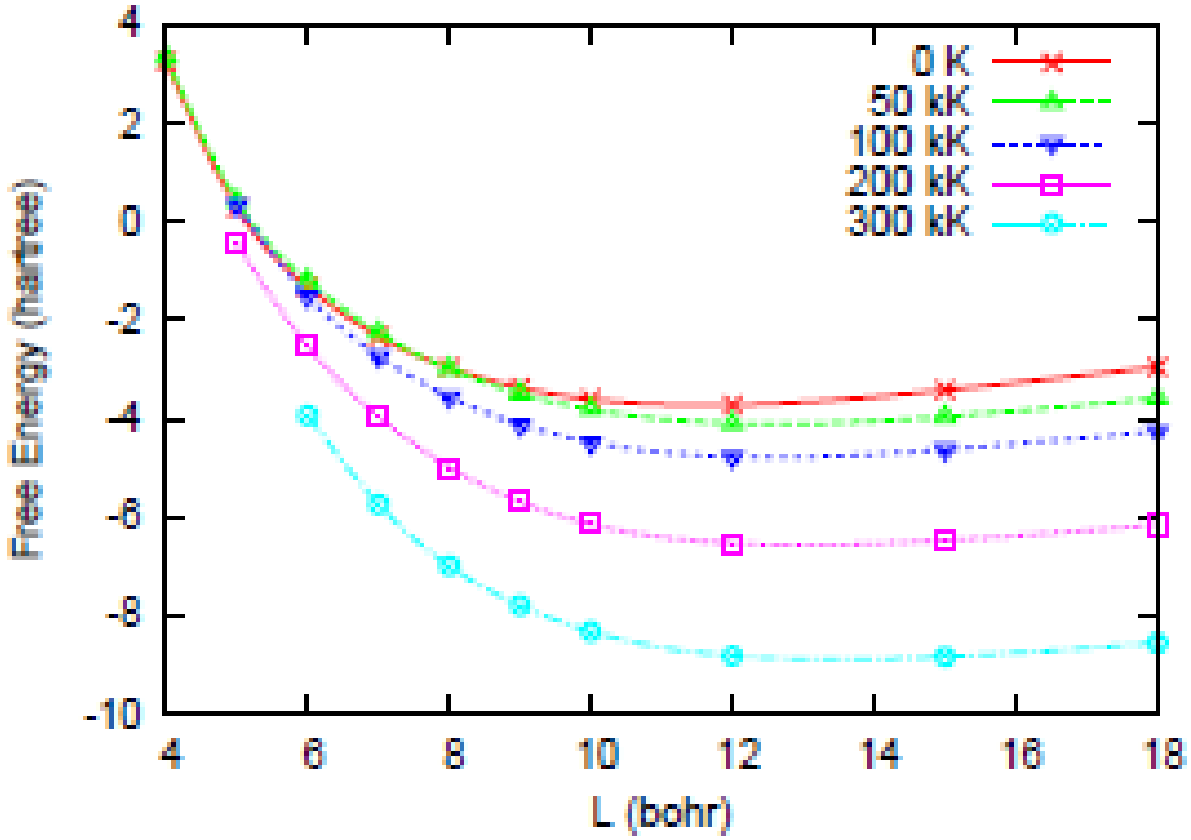
**Initial ion configuration. Each ion is at the center of its own octant. Relative geometry is constrained as *L* is scaled.**

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



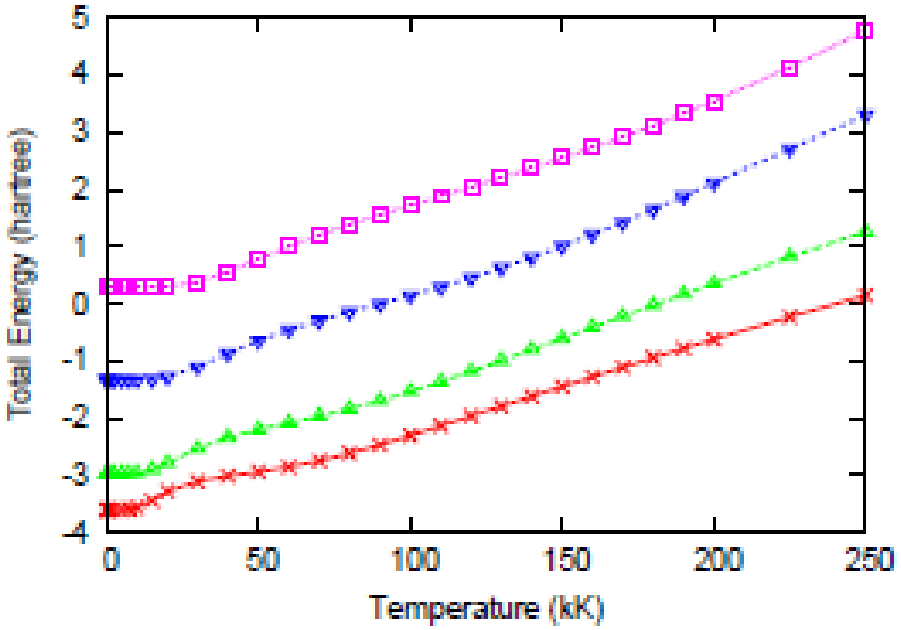

***Total*** **energy as a function of *L* for zero and finite *T*. The ion configuration has each ion at the center of its own octant.**

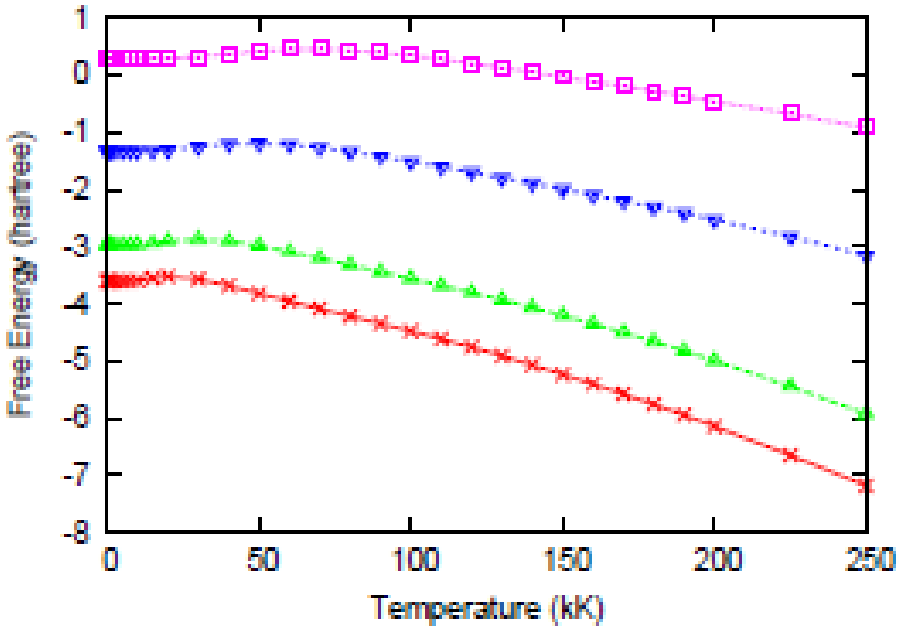
## *8 Atom Array of Cubical Symmetry in a Cubical Box - continued*




***Free*** **energy as a function of *L* for zero and finite *T*. The ion configuration has each ion at the center of its own octant.**

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




**Total energy and free energy as functions of *T* for four *L* values.**

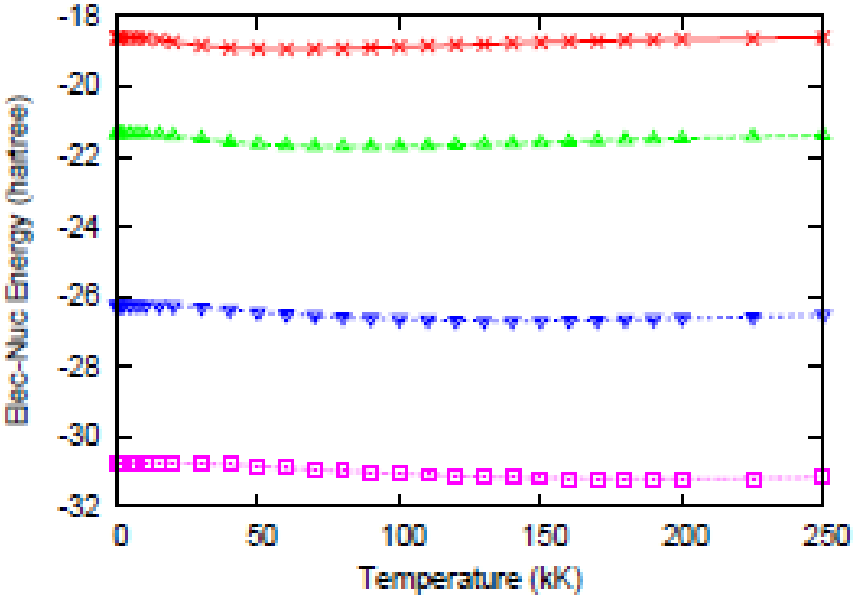
□ □ □ □ □ *L* = 5 bohr

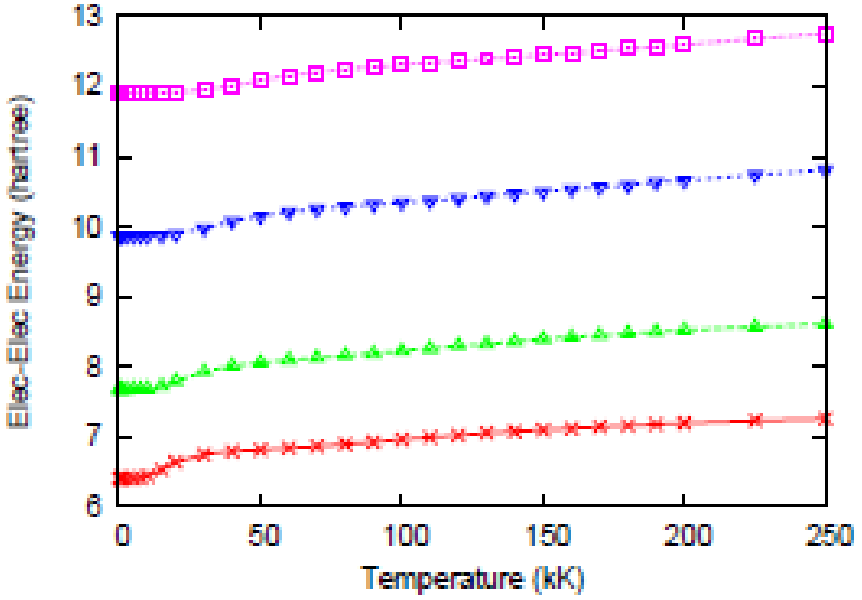
▽▽▽▽▽ *L* = 6 bohr

△△△△△ *L* = 8 bohr

×××××  *L* = 10 bohr

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




**$E_{electron\text{-}nuclear}$ and $E_{electron\text{-}electron}$ as functions of *T* for four *L* values.**

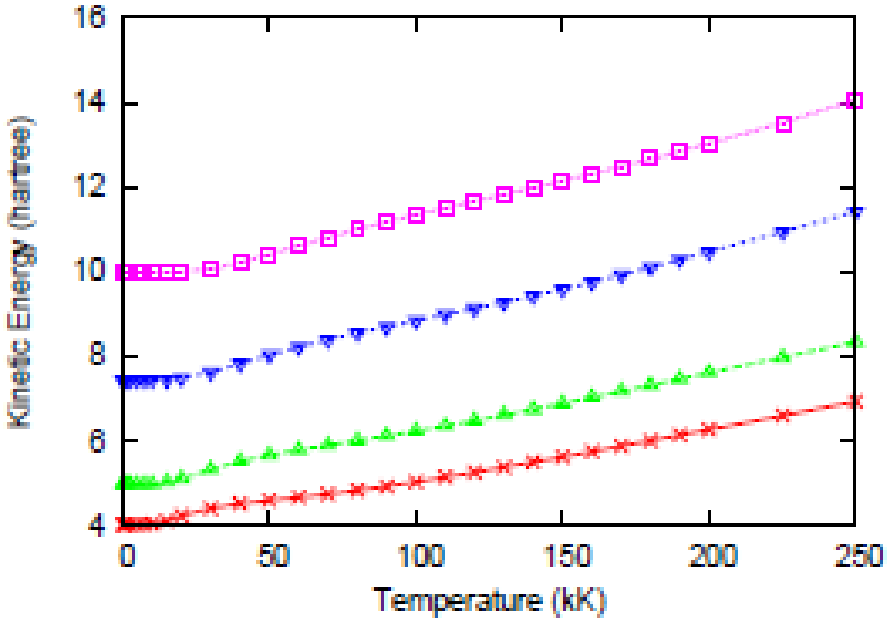
□ □ □ □ □ ***L* = 5 bohr**

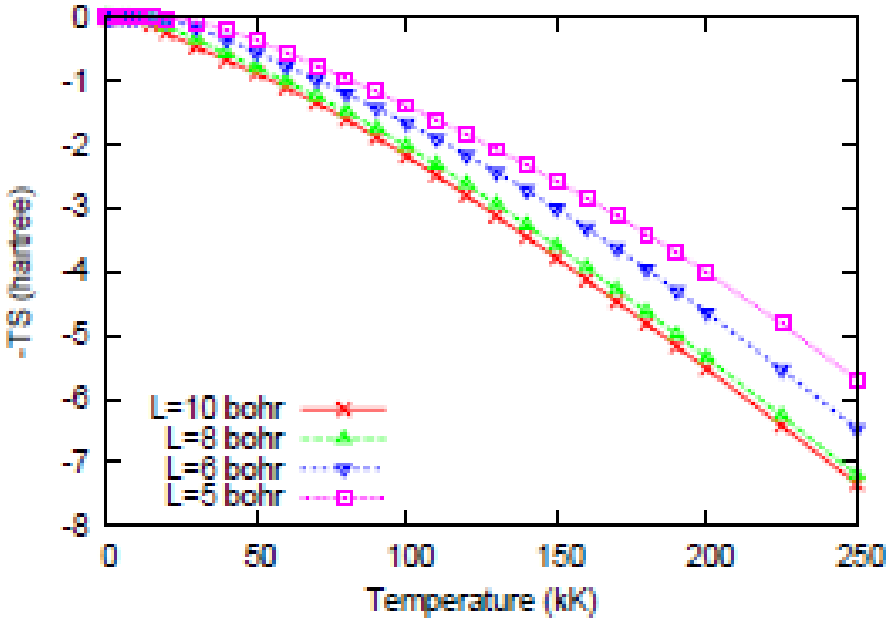
▽▽▽▽▽ ***L* = 6 bohr**

△△△△△ ***L* = 8 bohr**

×××××  ***L* = 10 bohr**

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



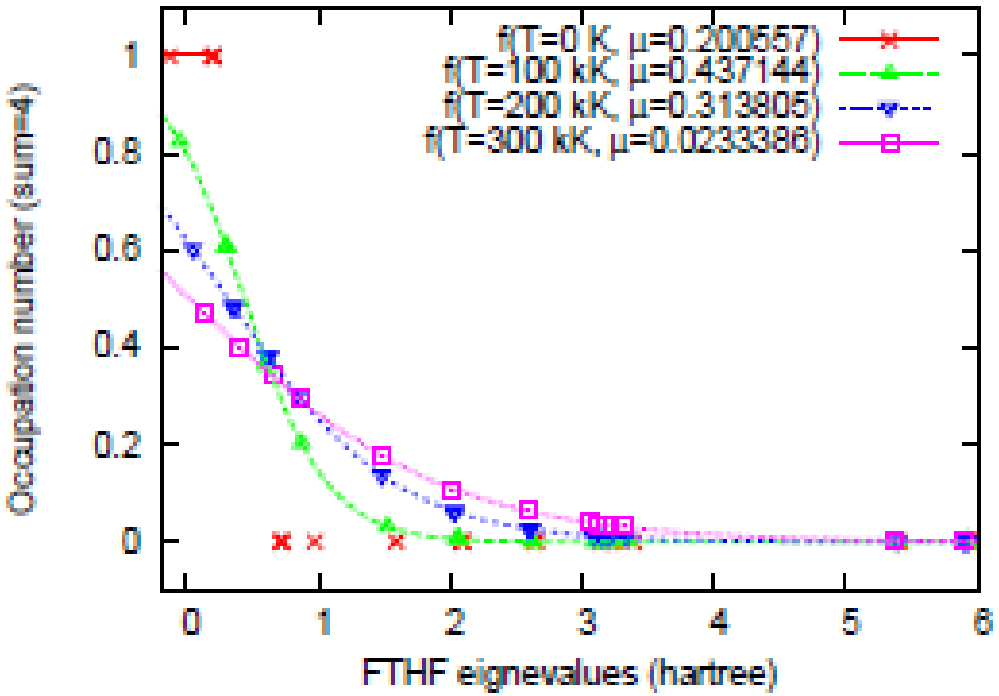




**KE and -*TS* as functions of *T* for four *L* values.**

□ □ □ □ □ *L* = 5 bohr ▽▽▽▽▽ *L* = 6 bohr

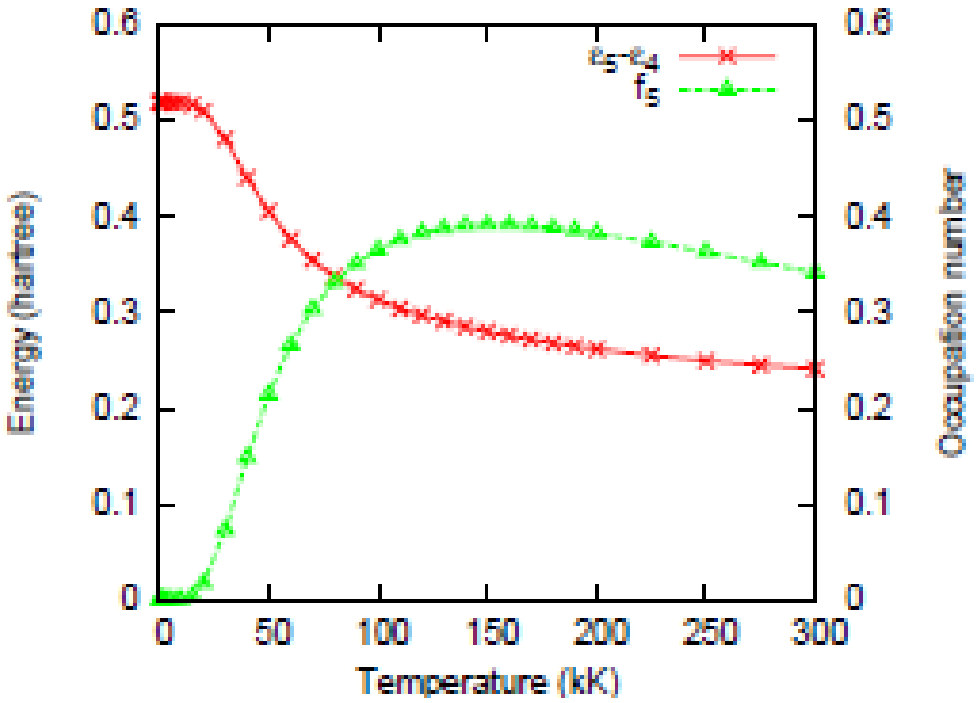
△△△△△ *L* = 8 bohr ××××× *L* = 10 bohr

# 8 Atom Cubical Array – What are those 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*.**

# 8 Atom Cubical Array – What are those plateaus?

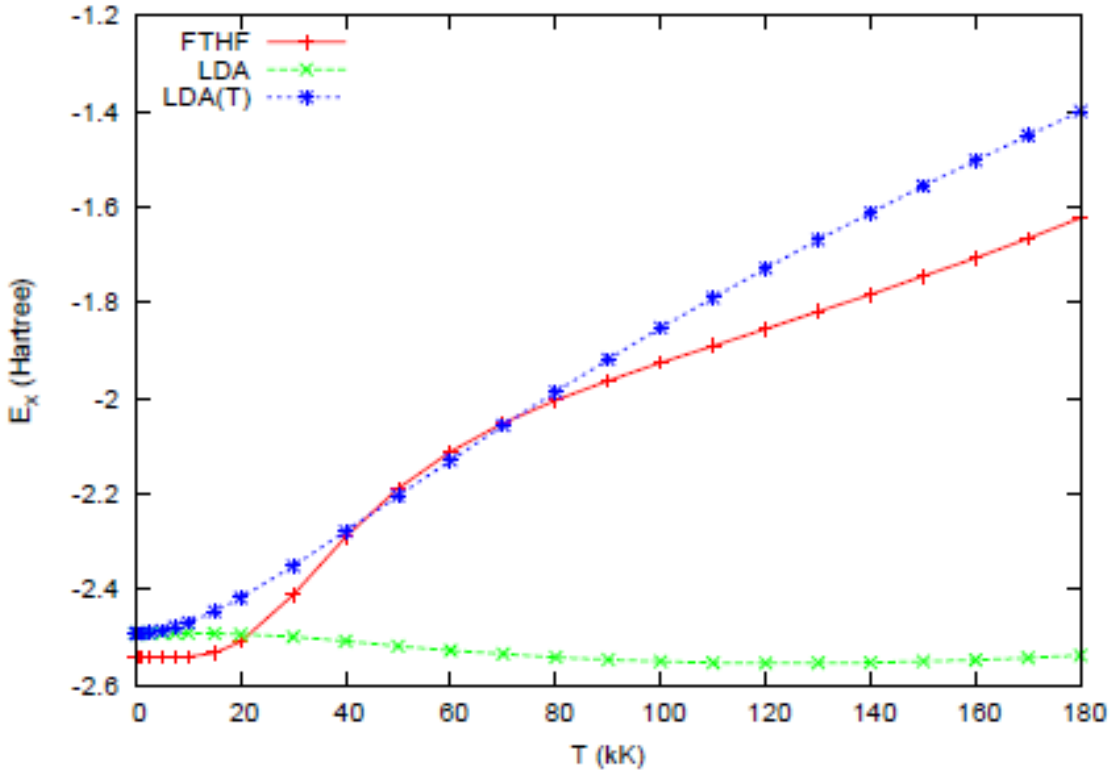



**Orbital eigenvalue difference $\varepsilon_5 - \varepsilon_4$**

**Fermi occupation number for orbital 5**

**Temperature-induced population causes reduction in self-repulsion of orbitals that are unoccupied (virtual) in the ground state. ⇒ Challenge for builders of orbital-free density functionals .**

# 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**

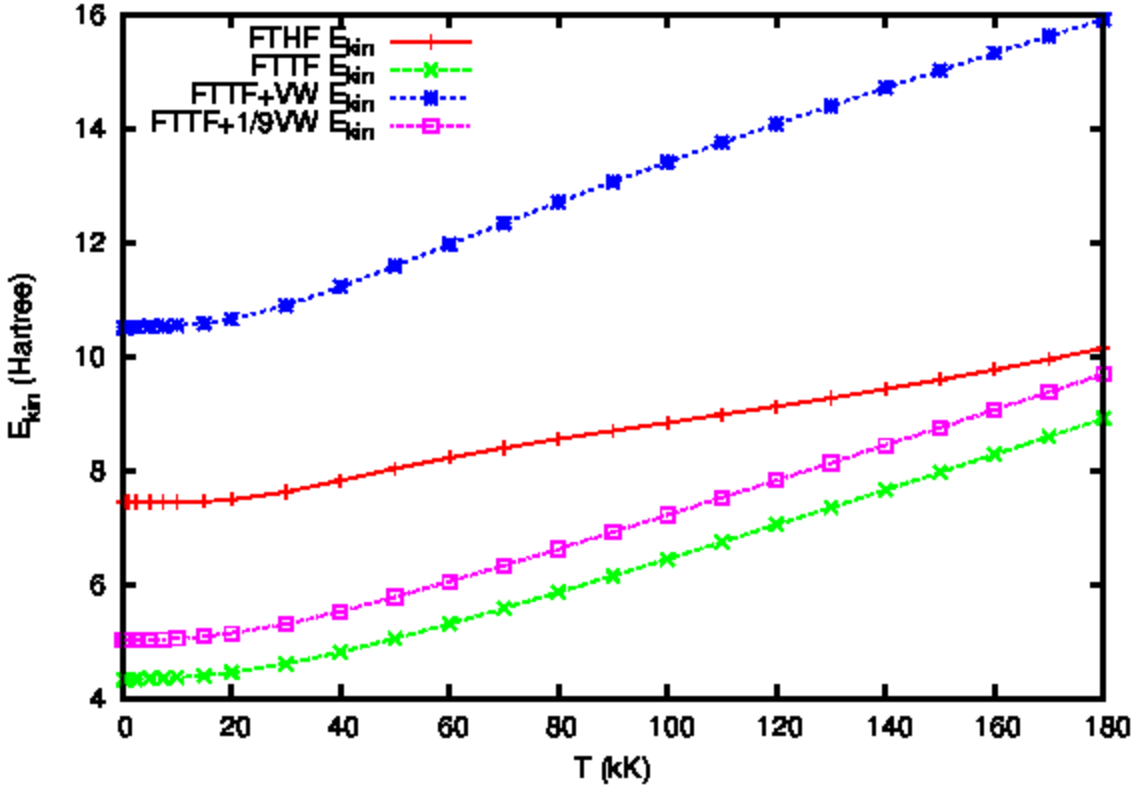
## Orbital-free KE – Thomas-Fermi and von Weizsäcker Functionals

$$T_{FTTF\,\lambda W}[n] := T_{FTTF} + \lambda_W T_W \quad , \qquad 0 \le \lambda_W \le 1$$

$$T_{FTTF}[n] := \frac{\sqrt{2}}{\pi^2 \beta^{5/2}} I_{3/2}(\beta\mu) \quad , \quad I_n(y) = \int_0^\infty \frac{x^n}{1+e^{(x-y)}} dx$$

$$T_W[n] := \frac{1}{8} \int d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

## *Comparison of Kinetic Energy Functionals*




$\lambda_W = 1$

*HF*

$\lambda_W = 1/9$

$\lambda_W = 0$

$E_{kin}$ **from finite-temperature Hartree-Fock (FTHF).**

$E_{kin}$ **from finite-temperature Thomas-Fermi FTTF density.**

$E_{kin}$ **from FTTF + temperature-independent von-Weizsacker gradient correction.**

$E_{kin}$ **from FTTF + temperature-independent second gradient correction.**

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

## *Summary -*

- Testing and construction of finite-temperature functionals needs constraints and fiduciary data from well-defined model systems.
- We have developed and implemented a scheme for first-principles calculations in a well-defined approximation (Thermal Hartree-Fock) applied to a simple warm dense matter system.
- Contributions to the free energy are smooth in $T$ once the ground state virtual orbitals are populated enough to move them down (reduce artificial self-repulsion of virtuals in HF).
- A simple non-self-consistent comparison shows that FTHF $E_x[\, n,T\,]$ is not well-modeled by ground-state LDA but is at least roughly reproduced by $T$-dependent LDA exchange. $E_{kin}[\, n,T\,]$ approximations do not fare as well.
- Application to more complicated ion arrangements is underway.
- Resulting data will be used to test both existing free energy density functionals and those we are constructing.

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