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

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Topics

- Motivation: Simulation of the Physics of Warm Dense Matter

- Review: Finite-temperature, Orbital-free Free Energy Density Functionals
  - Objectives:

    Practical - drive molecular dynamics

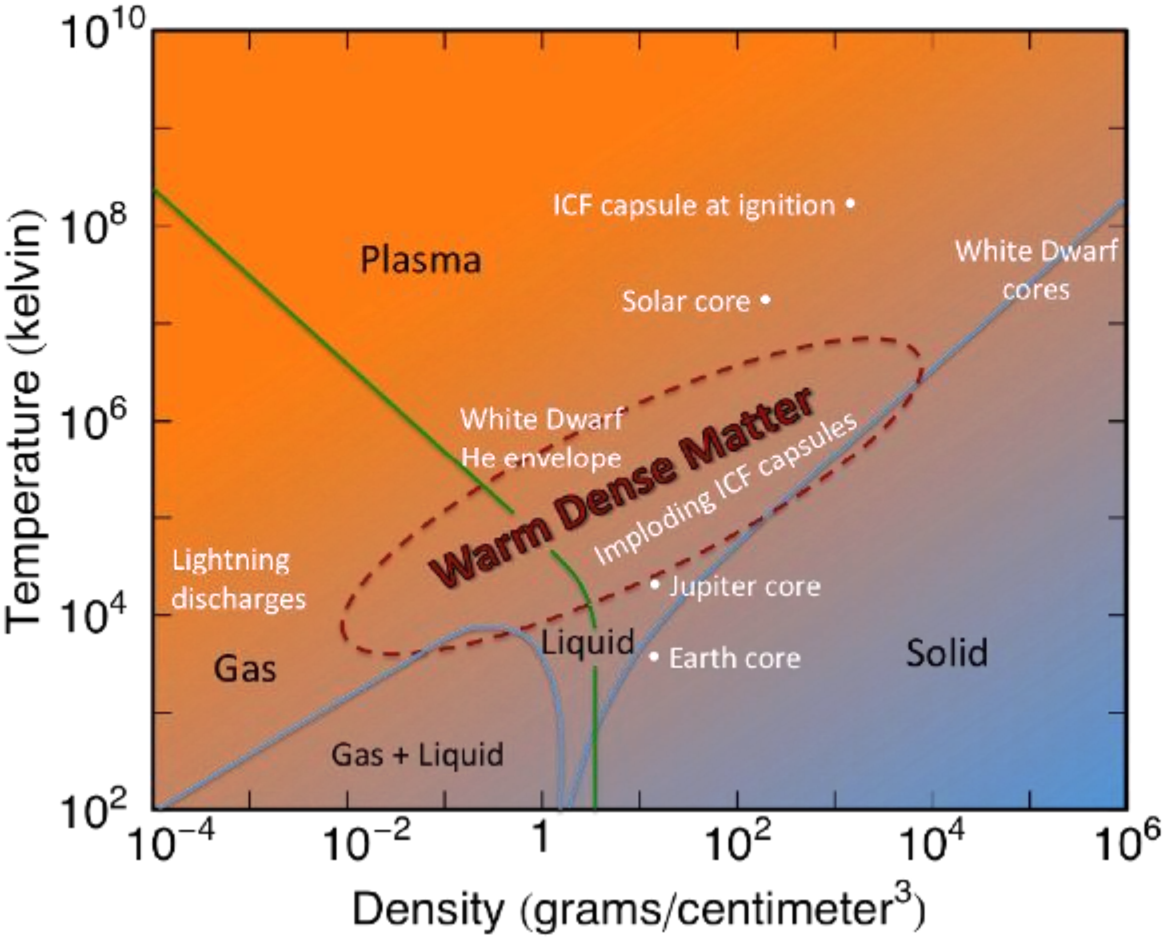
    Conceptual – realize fundamental content of DFT
  - Kohn-Sham kinetic energy contribution
  - Kohn-Sham entropy contribution
  - Exchange-correlation free energy
  - Implicit T dependence of ground-state functionals

- Challenge: Scarcity of data for finite-temperature, inhomogeneous, many-electron systems.

- Response: Thermal Hartree-Fock calculations on confined, many-electron systems (= this talk).

Warm Dense Matter

Warm dense matter $0 \le T \le 1{,}000{,}000$ K . Densities from gas to highly compressed solid-like.



Warm Dense Matter – Why the Interest?

- **Violent formation of planets – *platforms for life***
  - **late-stage giant impacts, Moon formation**
  - **evolution of planets, magnetic fields**
- **Path to stars – *nuclear ignition***
  - **giant to supergiant planets (exo-planets) to brown dwarfs**
  - **path to ignition in the laboratory**
- **Extreme chemistry**
  - **Periodic Table transformed**
  - **“hot ices” (molecular systems), alloys and compounds**

►◄►◄►◄►◄

Properties of warm dense matter

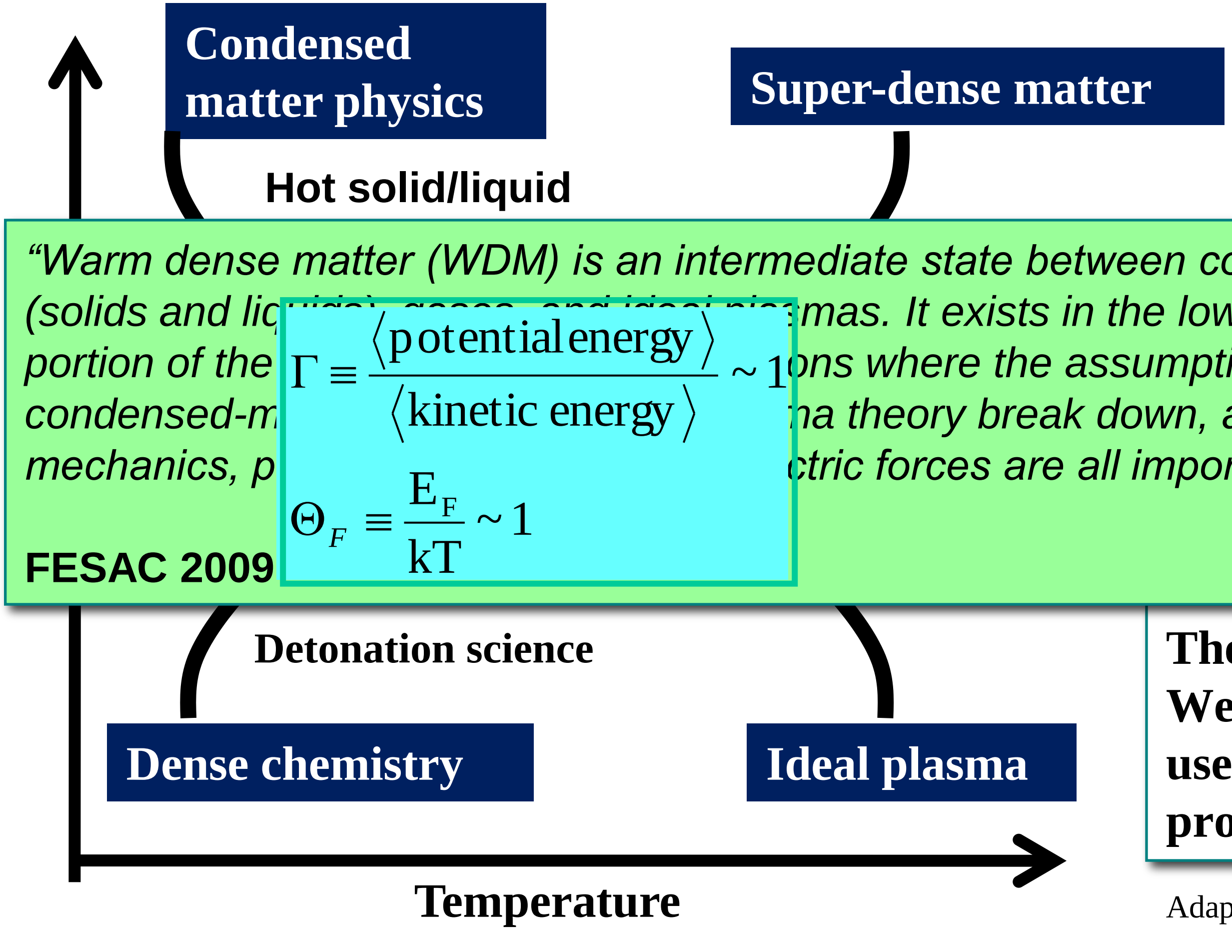
– **solids at ultra-high pressures or in ultra-high magnetic fields**
– **melting at extreme compression**
– **liquid–liquid, plasma phase transitions**
– **transport properties**

- **Example application: Hypervelocity impact threats**
  - **satellite protection**
  - **killer asteroids**

Warm Dense Matter Panel, High Energy Density
Laboratory Plasma ReNew Workshop; Nov. 2009

Warm Dense Matter – the Challenge

Warm dense matter regime is the meeting ground of several distinct physical regimes- a scientifically rich area of High Energy Density Plasmas



Condensed matter physics

Super-dense matter

Hot solid/liquid

“Warm dense matter (WDM) is an intermediate state between condensed matter (solids and liq … mas. It exists in the lower-temperature portion of the … ons where the assumptions of both condensed-m … na theory break down, and where quantum mechanics, p … ctric forces are all important.”

FESAC 2009

$$\Gamma \equiv \frac{\langle \text{potential energy} \rangle}{\langle \text{kinetic energy} \rangle} \sim 1$$

$$\Theta_F \equiv \frac{E_F}{kT} \sim 1$$

Detonation science

Dense chemistry

Ideal plasma

Temperature

The WDM challenge: Well- developed models used on WDM face severe problems

Adapted from F. Graziani, Nov. 2009 ,
from R. More, WDM School, LBNL, 2008

Topics

- **Motivation: Simulation of the Physics of Warm Dense Matter**
- **Review: Finite-temperature orbital-free Free Energy Density Functionals**
  - **Objectives:**

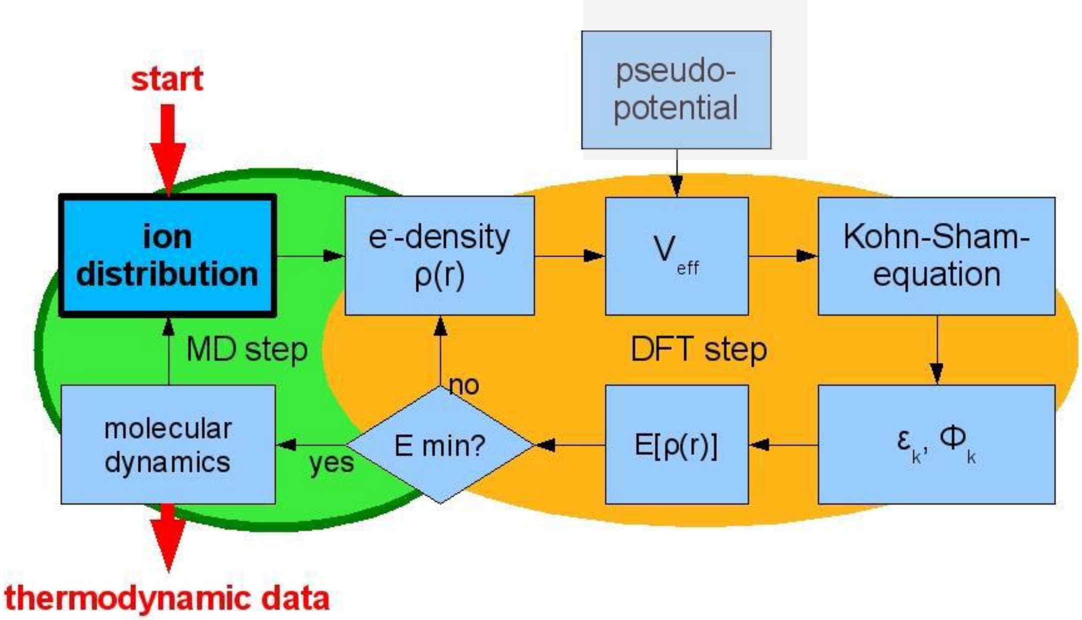
    Practical - drive molecular dynamics
    Conceptual – realize fundamental content of DFT
  - **Kohn-Sham kinetic energy contribution**
  - **Kohn-Sham entropy contribution**
  - **Exchange-correlation free energy**
  - **Implicit T dependence of ground-state functionals**
- **Challenge: Scarcity of data for finite-temperature, inhomogeneous, many-electron systems.**
- **Response: Thermal Hartree-Fock calculations on confined, many-electron systems (= this talk).**

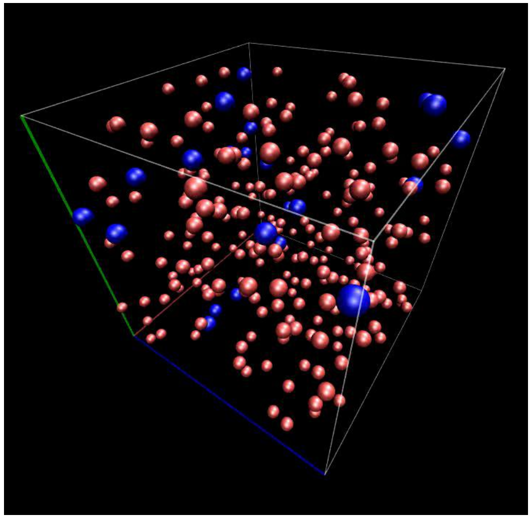
WDM Systems and Simulation Bottleneck

Molecular dynamics is the dominant simulation tool in materials physics. 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 . It should be the Born-Oppenheimer free- energy surface

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





H-He (8.6%) @ 1 Mbar, 4000 K

$\mathcal{F}(\{\mathbf{R}\})$ is the *electronic* free energy.

Quantum Stat Mech → $ $ $ $ or € € € € €

Adapted from R. Redmer, LBNL WDM, 2011

Many-electron Hamiltonian

The N_e -electron Hamiltonian of real systems in the B-O approximation is:

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

$$:= \hat{\mathcal{T}} + \hat{V}_{ee} + \hat{V}_{ion}$$

$$:= \hat{H}_{ee} + \hat{V}_{ion}$$

Hartree atomic units:

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

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

One-electron KE: $\tfrac{1}{2}\int d\mathrm{r}\,\left|\nabla\phi\right|^2$

Free Energy Density Functional Theory

Mermin-Hohenberg-Kohn finite-temperature DFT
(For warm dense matter $0 \leq T \leq 1{,}000{,}000$ K) Basic equations are:

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

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

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

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

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

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

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

$$\beta = 1/k_B T$$

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

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 $\leq$ M $\leq$ 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?

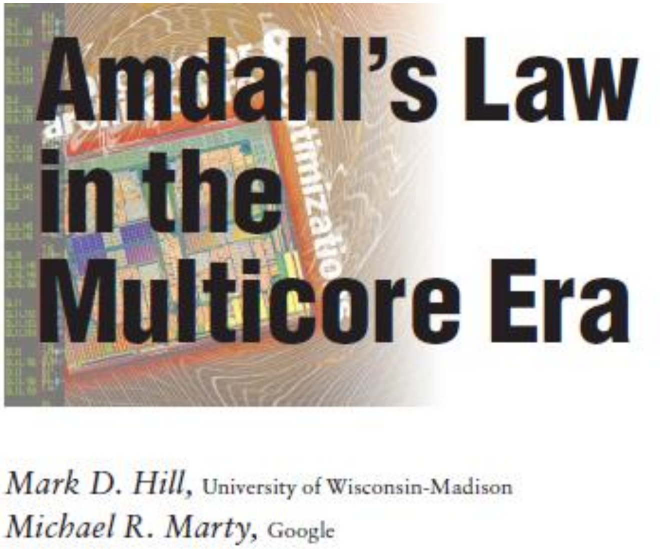
"Everyone knows Amdahl's Law but quickly forgets it"

T.Puzak, IBM (2007)

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

99.9 % parallel, 2048 processors , speedup ≈ 675

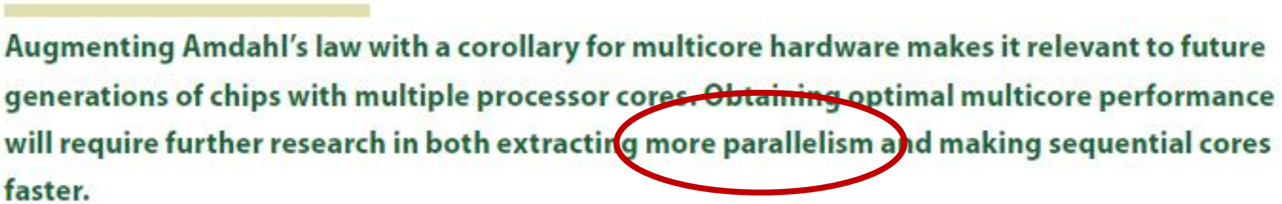
S = speedup; P = fraction parallel; N = number of processors



Amdahl's Law in the Multicore Era

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

IEE Computer, 41, 33 (2008)



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.

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

The Ideal - Orbital-free DFT

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

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

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

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

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

DFT for WDM – Major Open Questions

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

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

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

Functional forms for $t_S[n, T]$, $s_S[n,T]$?

- **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?)**

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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 are:

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

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

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

$$\mathcal{T}_{HF}\left[\{\phi\}\right] := ½\sum_j f_j \int \mathbf{dr}\left|\nabla\varphi_j(\mathbf{r})\right|^2 \quad ; \quad \mathcal{S}_{HF}[\{\phi\}] := -k_B \sum_j \left[f_j \ln f_j + (1 - f_j)\ln(1 - f_j)\right]$$

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

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

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

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

Thermal Hartree-Fock Theory - continued

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

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

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

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**

($L \to \infty$).

- **Temperature range: $0 \le T \le 200{,}000$ K.**

Basis Set

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.

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

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

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

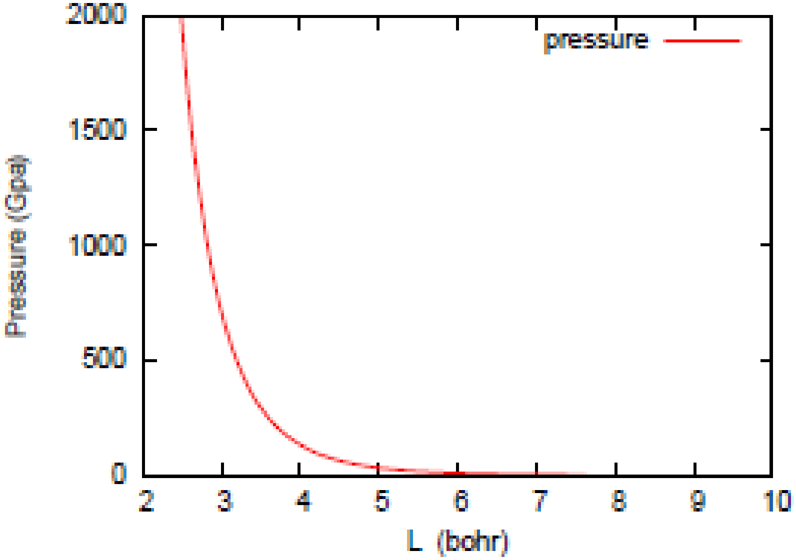
$$g^n(x;x_c) = (x - x_c)^n e^{-\alpha(x-x_c)^2}$$

Basis Set - continued

Technical issues and resolution:

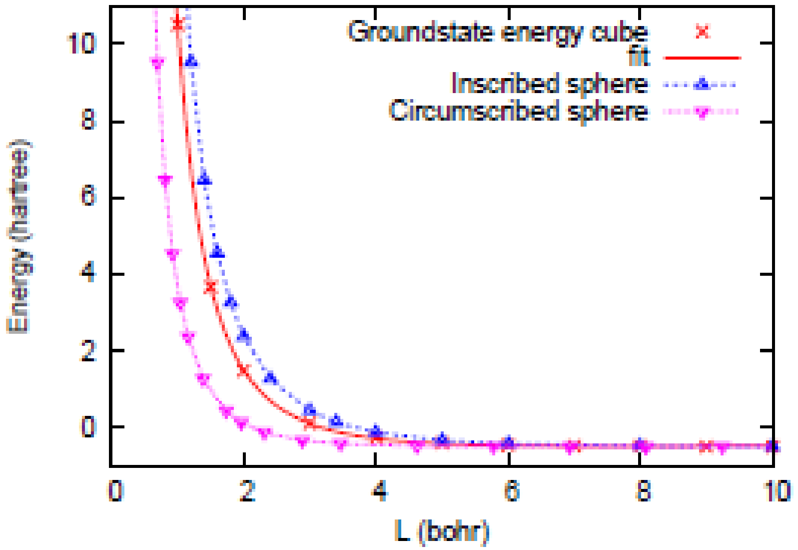
- **Continuity of first derivative at matching point and corrections to piecewise evaluation of KE matrix elements – works with a non-zero piece-wise correction for p-type functions**
- **Efficient calculation of 2- electron integrals – finite-range integrals of Gaussians and error functions done analytically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

Test Case - Single H Atom in a Cubical Box

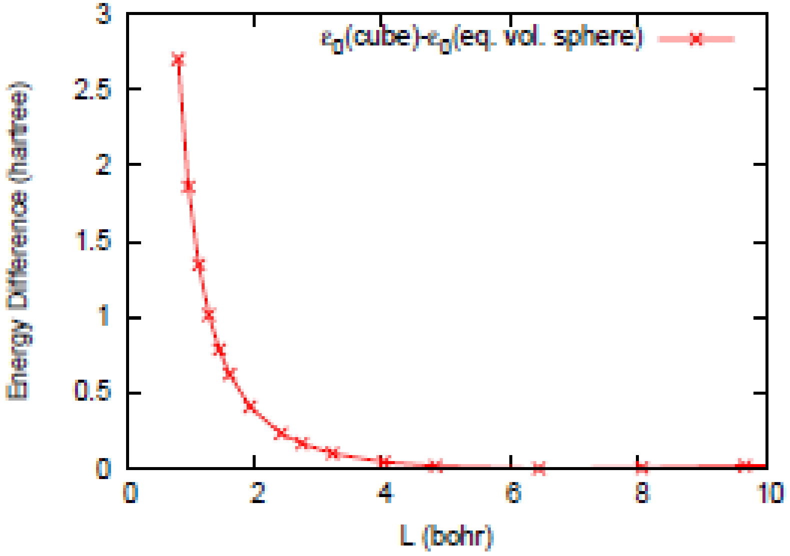


Ground-state pressure as a function of cube edge length.

Shape Matters! Single H Atom Confinement Shape Effects

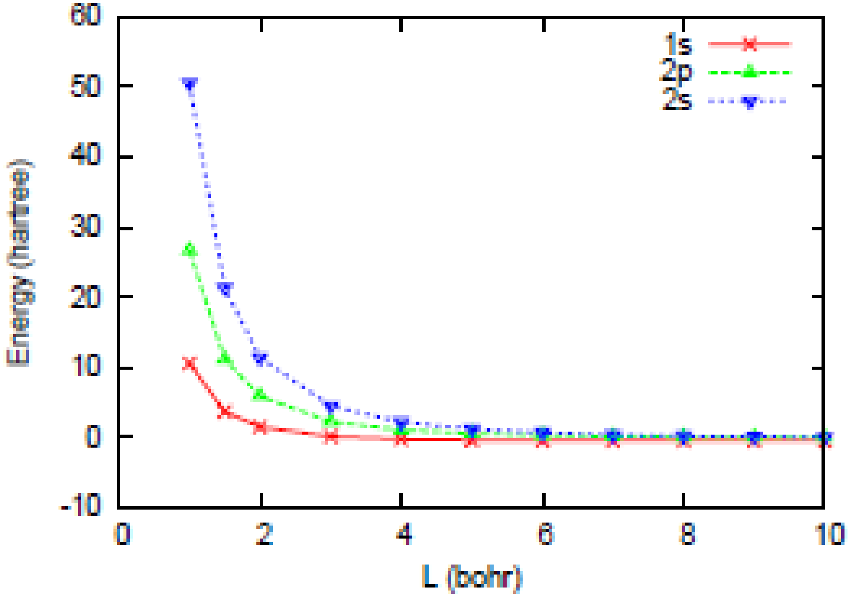


H atom ground state energy for cubic and bounding sphere confinements. Spherical data from Aquino et al. , Int. J. Quantum Chem. 107, 1548 (2007).

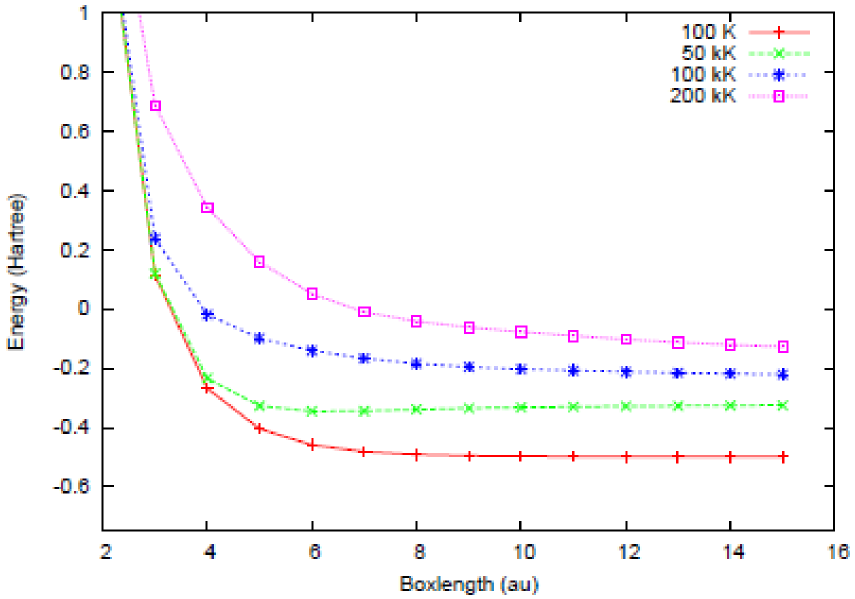


Difference between H atom ground state energy for cubic and equal-volume sphere confinements. Spherical data from Aquino et al. , Int. J. Quantum Chem. 107, 1548 (2007).

Test Case - Single H Atom in a Cubical Box (cont'd.)

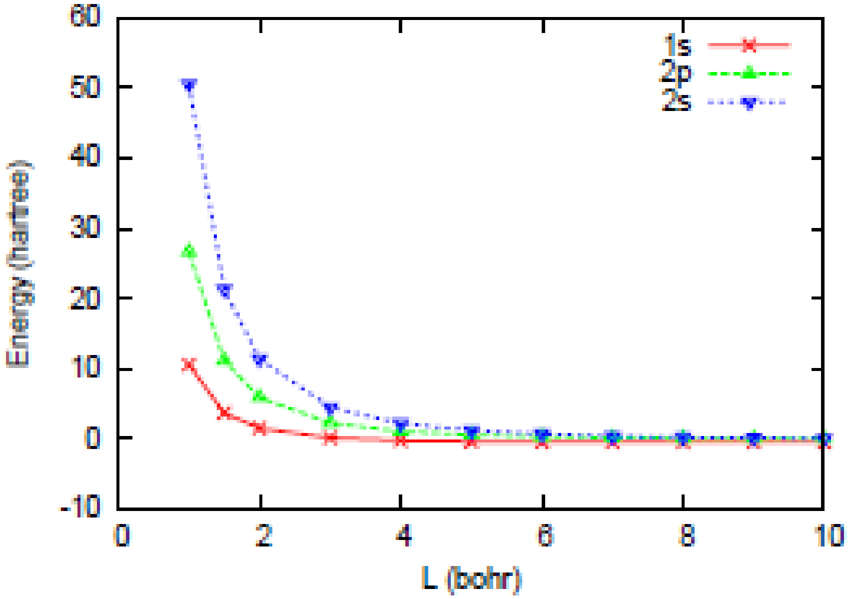


The 5 lowest eigenvalues for the single H atom in a box, (3 for 2*p*) as a function of *L*.

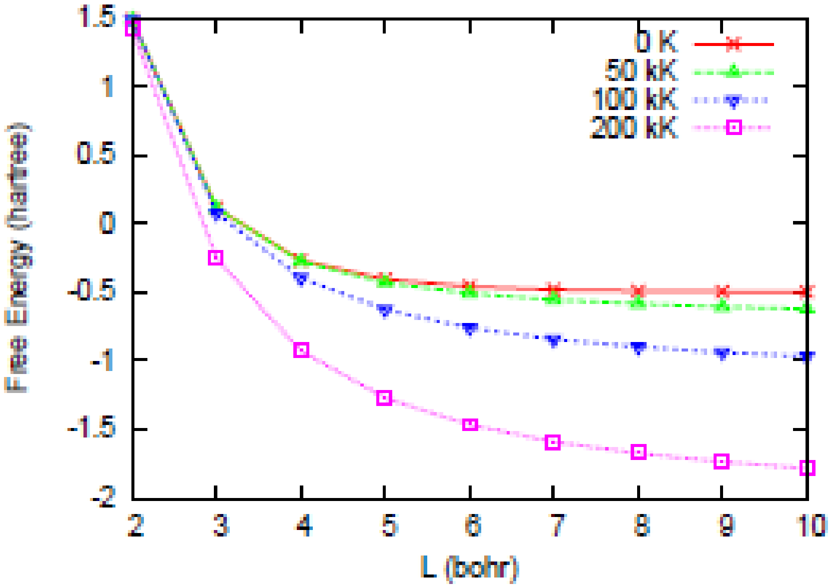


***Total* energy from thermal occupation of those eigenstates in the Fermi distribution as a function of *L* for four temperatures.**

Test Case - Single H Atom in a Cubical Box (cont'd.)

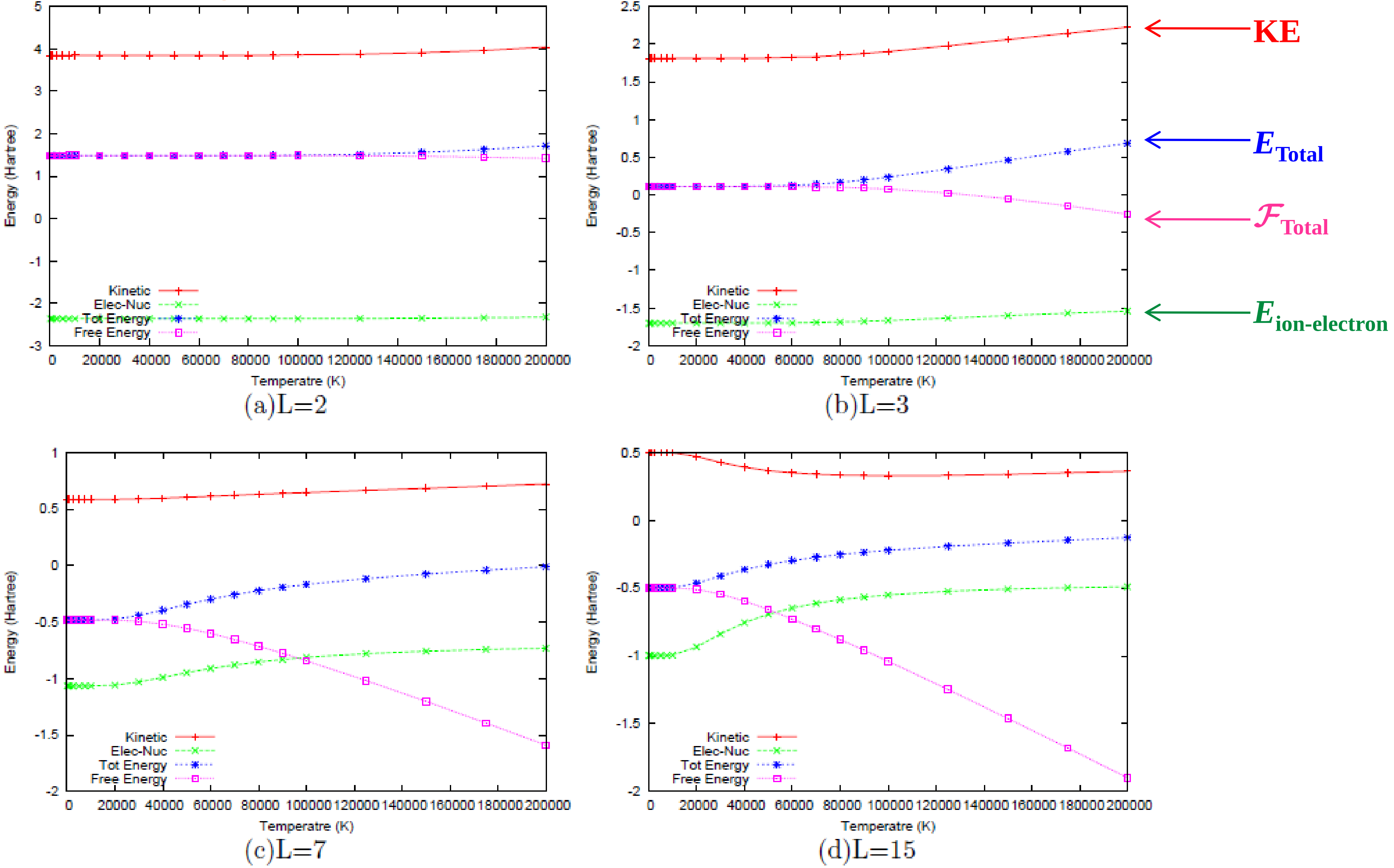


Repeat: The 5 lowest eigenvalues for the single H atom in a box, (3 for 2*p*) as a function of *L*.



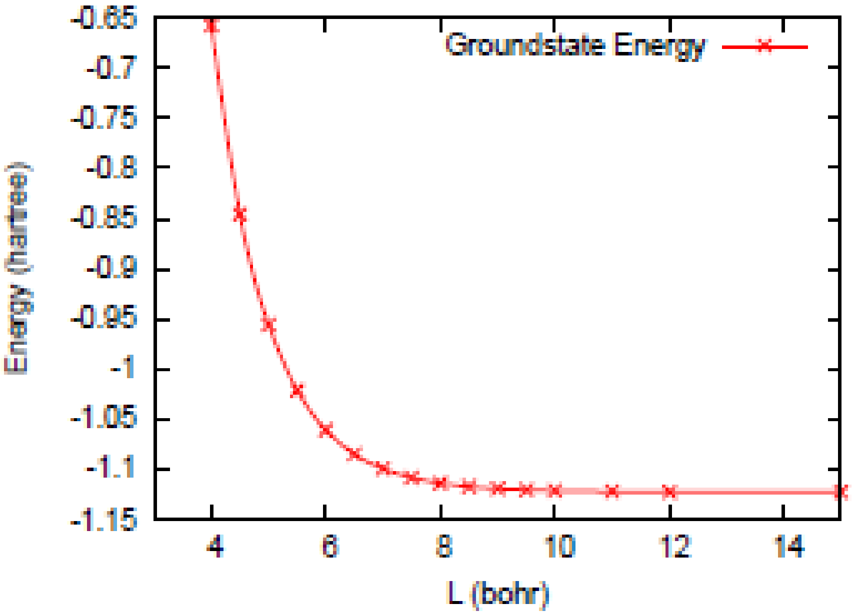
***Free* energy $\mathcal{F}$ from thermal occupation of those eigenstates in the Fermi distribution as a function of *L* for four temperatures.**

Test Case - Single H Atom in a Cubical Box (contd.)

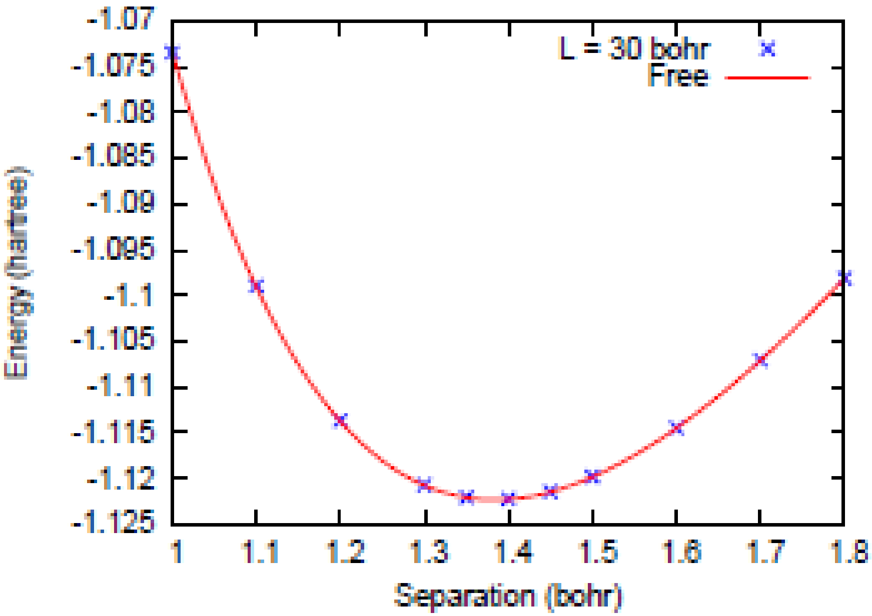


Total energy and free energy contributions for single H atom as functions of *T* for four values of *L* (bohr).

Test Case 2 - H_2 Molecule on the Body Diagonal of a Cubical Box



Ground state **energy of an H_2 molecule, bond length 1.4 au, centered in a cube with the atoms along the major diagonal vs. the cube edge length *L*.**



H_2 *ground state* energy as a function of bond length for the molecule on the body diagonal of an *L* = 30 au cube. Minimum at 1.383 au bond length, same as a free calculation using the same GTOs.

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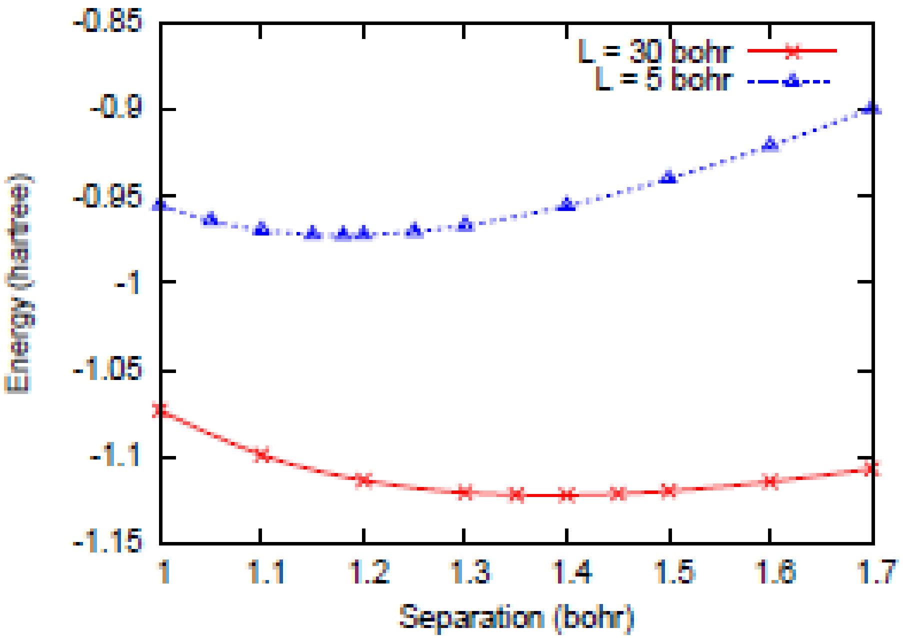
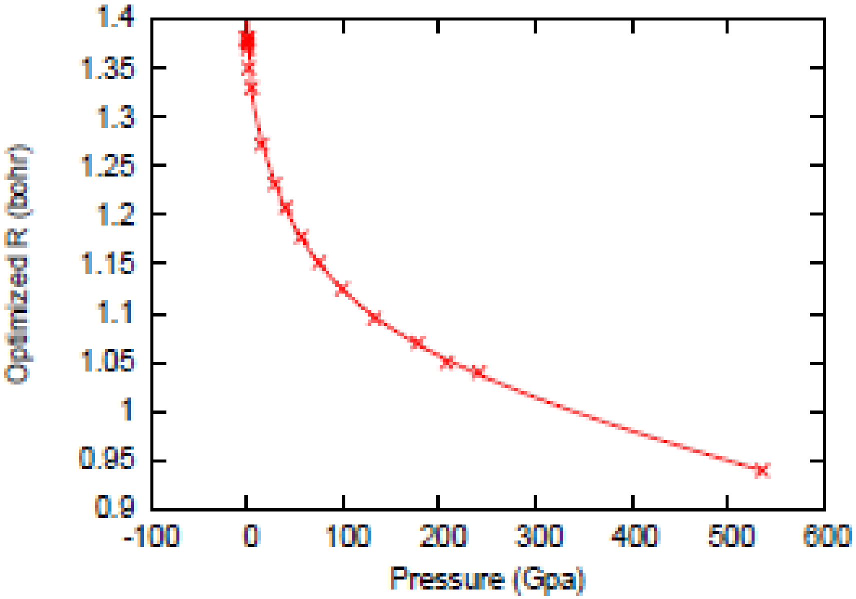
Test Case 2 - H_2 Molecule on the Body Diagonal of a Cubical Box

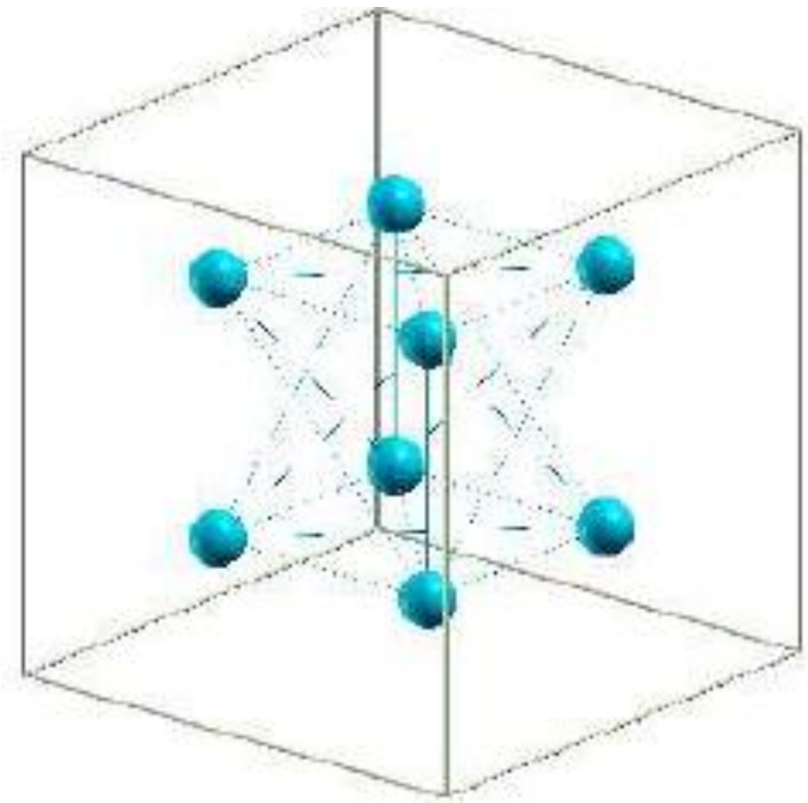


H_2 *ground state* energy as a function of bond length for the molecule on the body diagonal of *L* = 5 au and 30 au cubes. Minima at 1.18 and 1.38 au respectively.



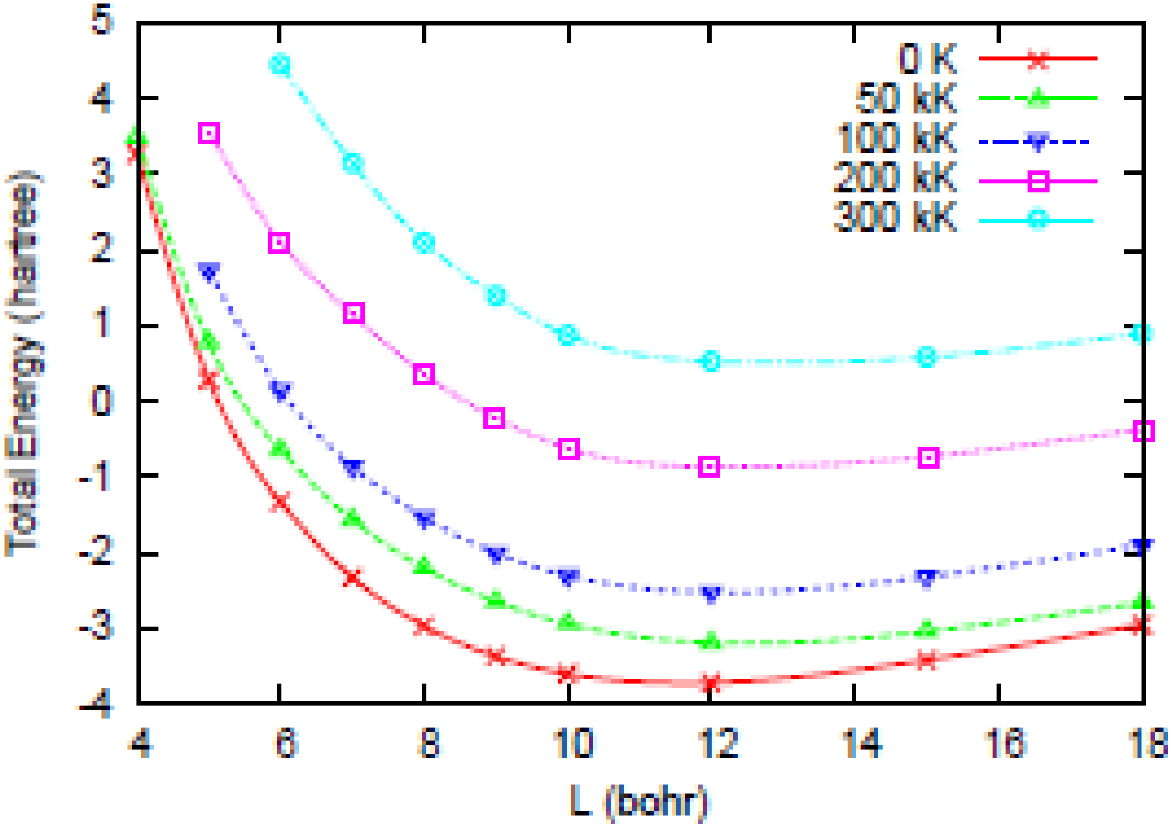
Optimized H_2 *ground state* bond length as a function of pressure.

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



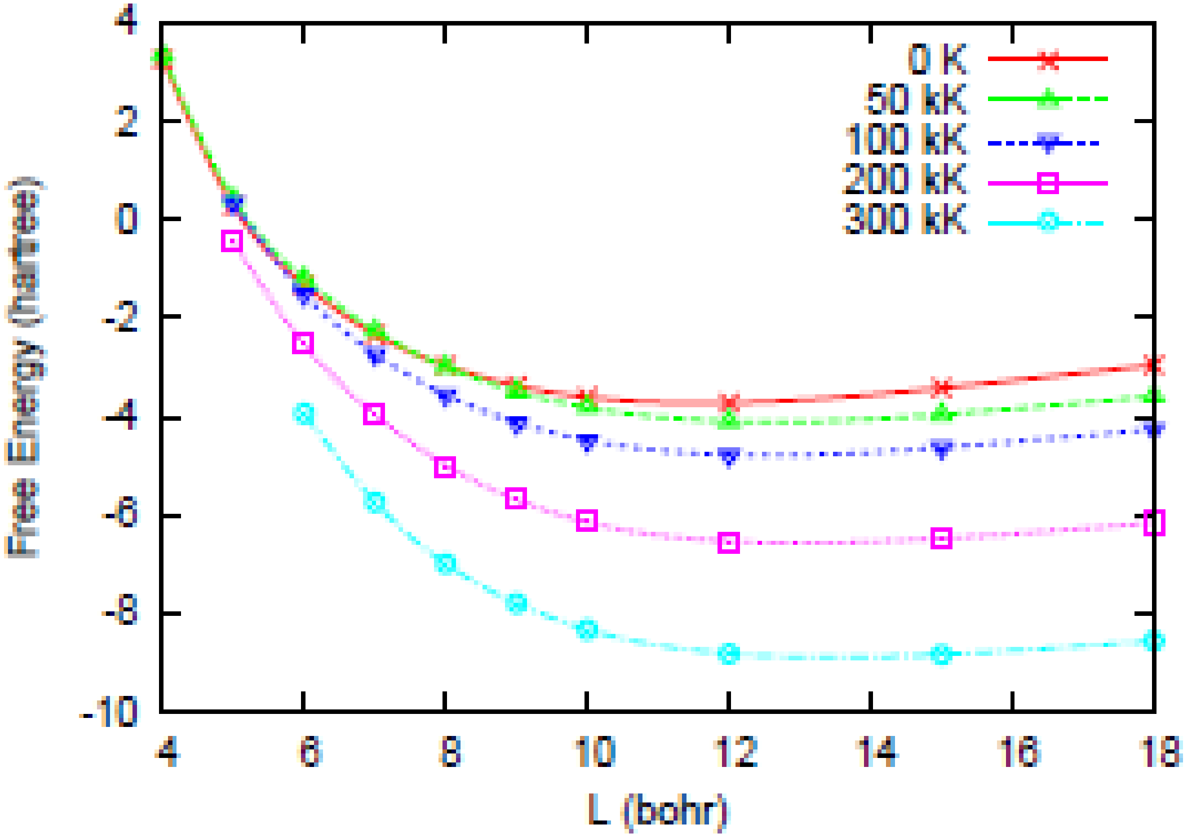
The ion configuration. Each ion is at the center of its own octant.

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



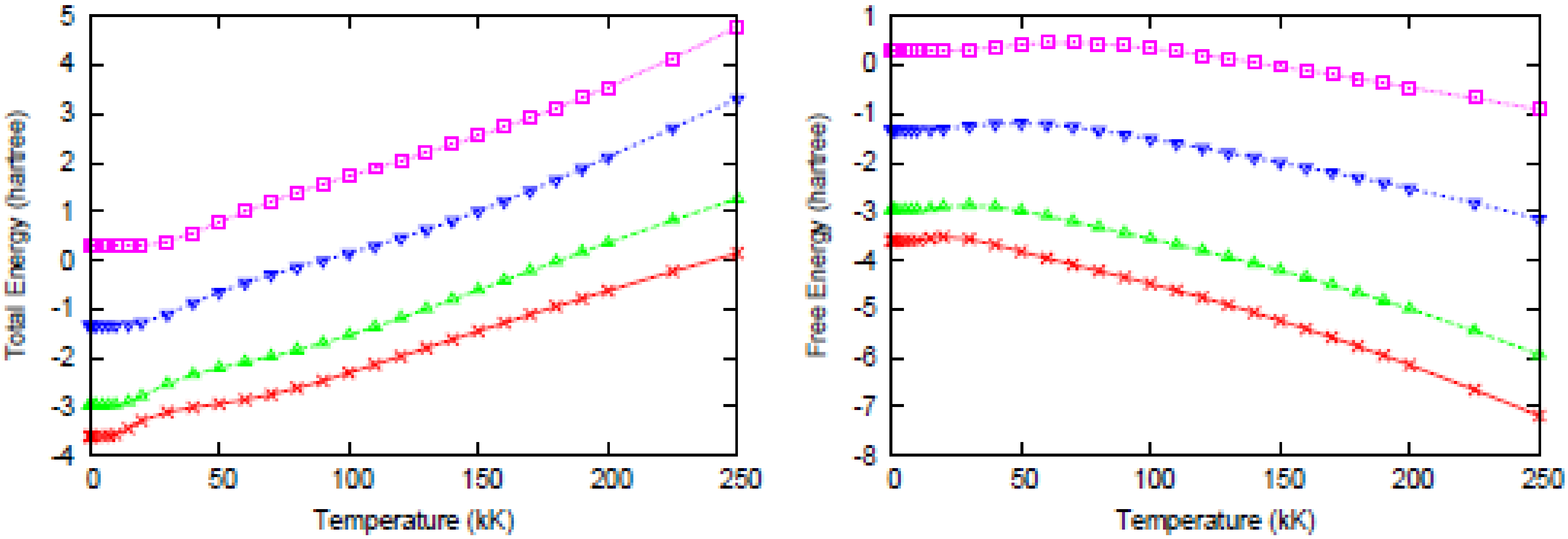
Total **energy as a function of *L* for zero and finite *T*. The ion configuration has each ion at the center of its own octant.**

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



***Free* energy $\mathcal{F}$ 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

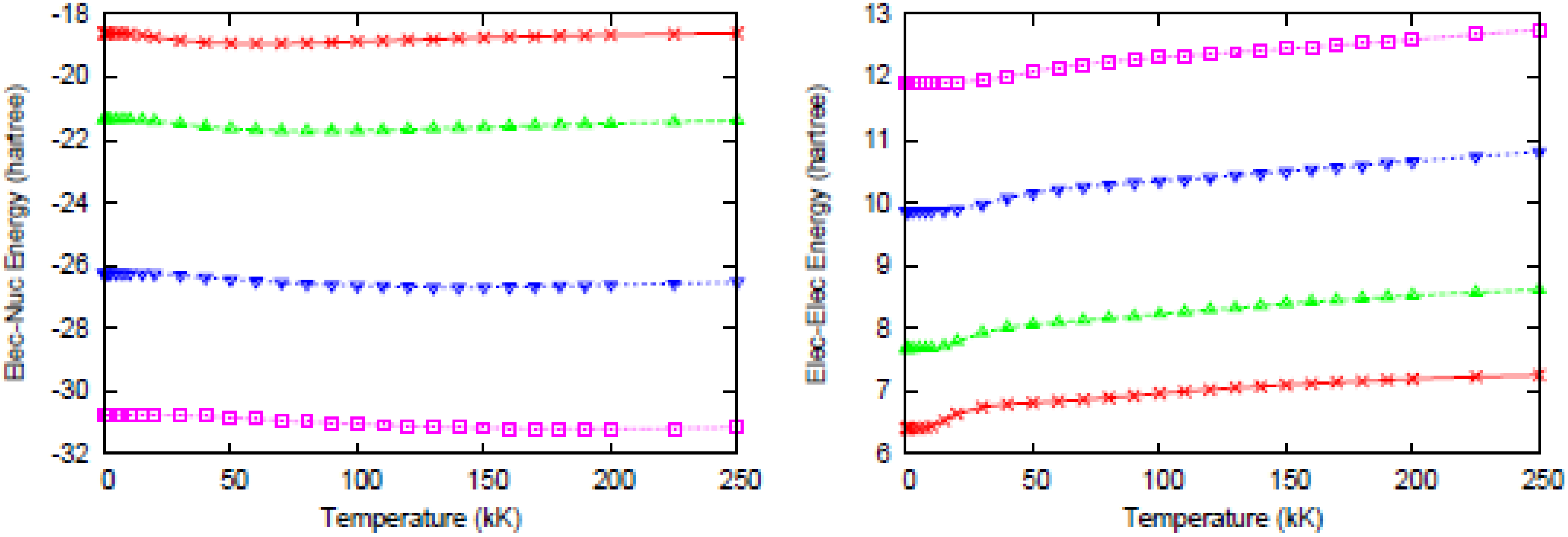


Total energy and free energy as functions of *T* for four *L* values.

□ □ □ □ □ *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.

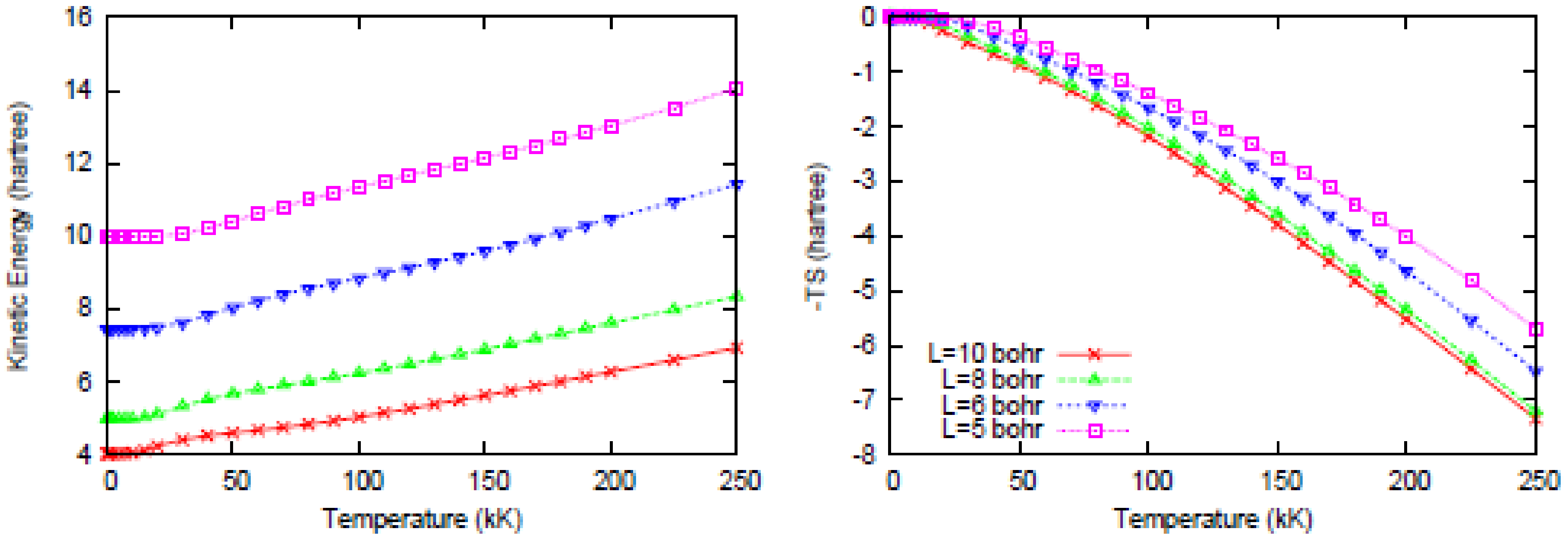
□ □ □ □ □ L = 5 bohr

▽▽▽▽▽ L = 6 bohr

△△△△△ L = 8 bohr

××××× L = 10 bohr

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

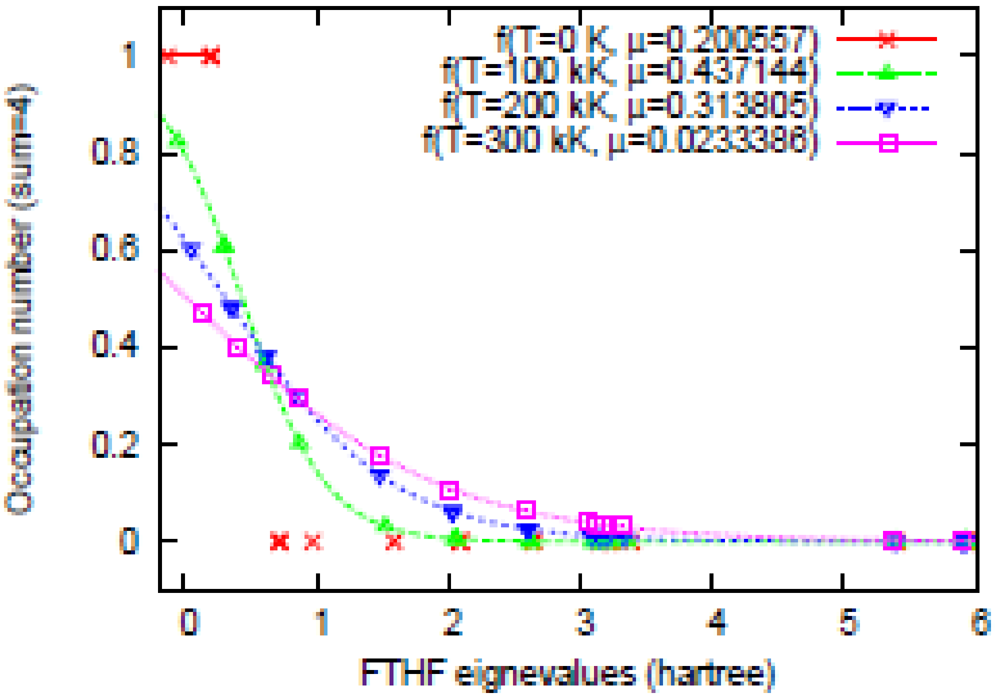


KE and -*TS* as functions of *T* for four *L* values.

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

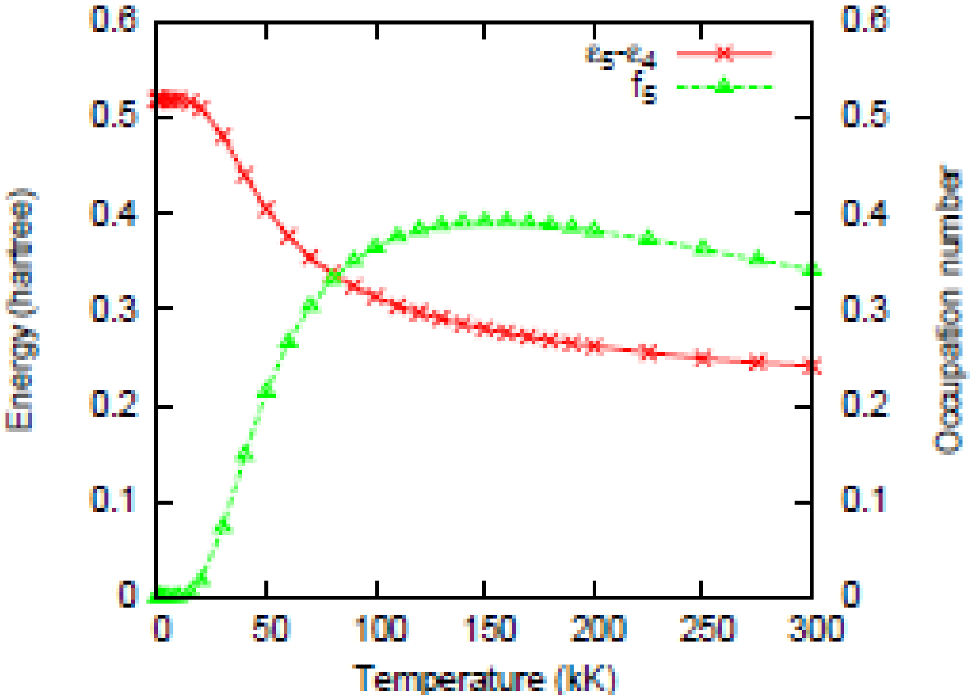
△△△△△ ***L* = 8 bohr** ××××× ***L* = 10 bohr**

8 Atom Cubical Array – What are those low-T plateaus?



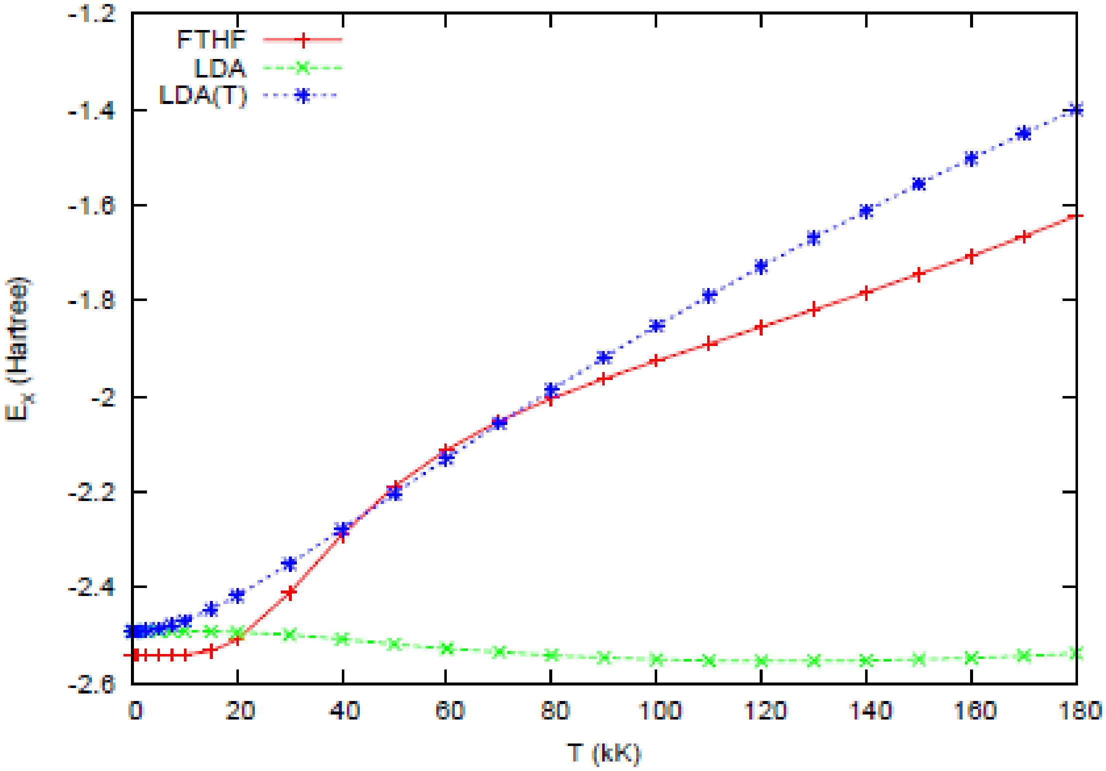
Fermi distribution for a <u>single</u> <u>spin</u> for four temperatures at *L* = 6 bohr. Note that the *T*=0 K occupied orbitals induced by cubic symmetry are a single *a1g* and a triply degenerate *t1u*.

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

Summary -

- **Testing and construction of finite-temperature functionals needs constraints and fiduciary data on 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 Perrot & Dharma-Wardana's 1984 paramaterization of T-dependent LDA.**
- **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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¡Gracias por su atención!

Credit: Bobby Scurlock