And now for something completely different

Kieron Burke

& many friends

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Value of approximations

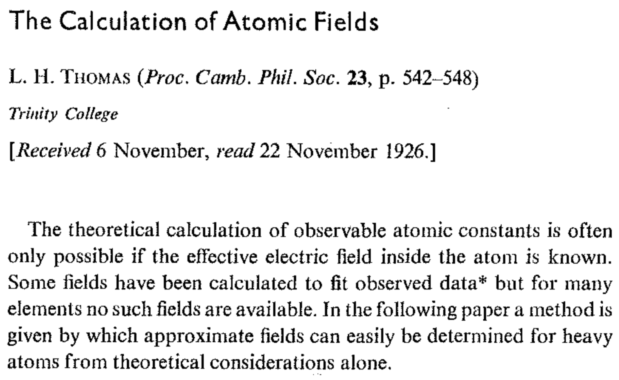
- *In any event, the result is extraordinarily powerful, for it enables us to calculate (approximate) allowed energies without ever solving the Schrödinger equation, by simply evaluating one integral. The wave function itself has dropped out of sight.*

- Griffiths, *Quantum Mechanics,* about *semiclassical* approximations.

Nature of the beast

- The most difficult problem I’ve ever worked on
- Possible payoffs
  - Understanding of asymptotic approximations
  - Complete transformation of society
- Explains many things about many areas
  - Semiclassical expansions
  - DFT and approximations like Thomas-Fermi
- Ties together
  - Math
  - Physics
  - Chemistry
  - Engineering and materials

Thomas/Fermi Theory 1926



The Calculation of Atomic Fields

L. H. Thomas (*Proc. Camb. Phil. Soc.* **23**, p. 542–548)

Trinity College

[*Received* 6 November, *read* 22 November 1926.]

The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.

- Around since 1926, before QM
- Exact energy: $E_0 = T + V_{ee} + V$
  - T = kinetic energy
  - V_{ee} = electron-electron repulsion
  - V = All forces on electrons, such as nuclei and external fields
- Thomas-Fermi Theory (TF):
  - $T \approx T^{TF} = 0.3\,(3\pi)^{2/3} \int d\mathbf{r}\; n^{5/3}(\mathbf{r})$
  - $V_{ee} \approx U$ = Hartree energy = $\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\; n(\mathbf{r})\, n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$
  - $V = \int d\mathbf{r}\; n(\mathbf{r})\, v(\mathbf{r})$
  - Minimize $E_0[n]$ for fixed N
- Properties:
  - Exact for neutral atoms as Z gets large (Lieb+Simon, 73)
  - Typical error of order 10%
  - Teller's unbinding theorem: Molecules don't bind.

Thomas-Fermi Theory Revisited

Elliott H. Lieb*
Institut des Hautes Etudes Scientifiques, 91440-Bures-sur-Yvette, France

and

Barry Simon†
Department of Physics, Eidgenössische Technische Hochschule, CH-8049 Zurich, Switzerland

(Received 8 June 1973)

We show that the Thomas-Fermi theory is exact for atoms, molecules, and solids as $Z \to \infty$.

Modern Kohn-Sham era

- 40's and 50's: John Slater began doing calculations with orbitals for kinetic energy and an approximate density functional for $E_{xc}[n]$ (called Xα)
- 1964: Hohenberg-Kohn theorem proves an *exact* $E_0[n]$ exists (later generalized by Levy)
- 1965: Kohn-Sham produce formally exact procedure and suggest LDA for $E_{xc}[n]$

Kohn-Sham equations (1965)

$$\left[-\frac{1}{2}\nabla^2 + \mathrm{v}_s[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} \left|\phi_i(\mathbf{r})\right|^2 =$$ ground-state density of interacting system

$$\mathrm{v}_s(\mathbf{r}) = \mathrm{v}_{\mathrm{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mathrm{v}_{\mathrm{xc}}[n](\mathbf{r})$$

$$\boxed{E_0 = T_S + V + U + E_{XC}[n]}$$

$$\boxed{\mathrm{v}_{\mathrm{xc}}[n](\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}}$$

Difference between T_s and E_{XC}

- Pure DFT in principle gives E directly from n(**r**)
  - Original TF theory of this type
  - Need to approximate T_S very accurately
  - Thomas-Fermi theory of this type
  - Modern orbital-free DFT quest
  - Misses quantum oscillations such as atomic shell structure
- KS theory uses orbitals, not pure DFT
  - Made things much more accurate
  - Much better density with shell structure in there.
  - Only need approximate $E_{XC}[n]$.

A little exercise

- Ignore e-e interaction – focus on T_s
- Reduce from 3d to 1d – can use WKB
- Eliminate Coulomb singularities – smooth potentials
- Use box boundary conditions – avoid turning points and evanescent regions

One particle in 1d

- WKB wavefunction has first two powers of $\hbar$:

$$\phi_E^{WKB}(x) \approx \frac{1}{\sqrt{p(x)}}\, e^{\pm i\,\theta(x)} \quad ,$$

where ($m = e^2 = 1$):

$$p(x) = \sqrt{2(E - v(x))} \qquad \theta(x) = \int_0^x dx'\, p(x')/\hbar \; .$$

- Exact for flat potential, $v(x) = 0$.
- Highly accurate for a slowly-varying potential.

N fermions in 1d

Suppose I have N (same-spin) fermions, and occupy the first N levels of the system. Is there a way to make a direct semiclassical approximation to *sums* over occupied orbitals? For example,

$$n(x) = \sum_{i=1}^{N} |\phi_i(x)|^2 , \qquad t(x) = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \phi_i^*(x)\phi_i''(x) ,$$

the density and kinetic energy density ($\phi'(x) = d\phi/dx$),

$$N = \int dx\, n(x) , \qquad T = \int dx\, t(x) ,$$

Rough sums

$$n(x) \approx \int_{-\infty}^{E_{\rm F}} \frac{dE}{\pi\hbar} \, |\phi_E(x)|^2 = \frac{k_{\rm F}(x)}{\pi} \, , \qquad k(x) = p(x)/\hbar \, ,$$

$$t(x) \approx \int_{-\infty}^{E_{\rm F}} \frac{dE}{\pi\hbar} \, [E - v(x)] \, |\phi_E(x)|^2 = \frac{\hbar^2 k_{\rm F}^3(x)}{6\pi} \, .$$

- Both $n(x)$ and $t(x)$ are determined solely by $v(x)$ and $E_{\rm F}$, i.e., local approximation in $v(x)$.
- Global condition to get $E_{\rm F}$ is normalization of $n(x)$:

$$\int dx \, n(x) = N \qquad or \qquad \theta_{\rm F}(\infty) = N\pi \, .$$

Inversion

One can invert the density equation and insert into $t(x)$ equation to find:

$$t^{\mathrm{loc}}(x) = \frac{\pi^2\hbar^2}{6}\, n^3(x),$$

which is the *local density approximation* to the non-interacting kinetic energy in 1d.
Knowing $T^{\mathrm{loc}}[n]$, one could solve the Euler equation:

$$\frac{\pi^2\hbar^2}{2}\, n^2(x) + v(x) = \mu \ ,$$

forgetting derivation of T^{loc}.

Higher orders

- Continuing the expansion to higher power of $\hbar$, we find, e.g.,

$$n(x) = \frac{k_{\mathrm{F}}(x)}{\pi}\left(1 + \frac{\hbar^2\, v''(x)}{48[E_{\mathrm{F}} - v(x)]^2} + \ldots\right) \;,$$

$$t(x) = \frac{\hbar^2 k_{\mathrm{F}}^3(x)}{6\pi}\left(1 + \frac{\hbar^2\, v''(x)}{16[E_{\mathrm{F}} - v(x)]^2} + \ldots\right) \;.$$

- Notice that expansion becomes accurate when $\hbar \to 0$ or $N \to \infty$, or $v(x)$ becomes constant.
- Inversion leads to the *gradient expansion* for T:

$$T^{GE}[n] = \frac{\pi^2\hbar^2}{6}\int dx\, n^3(x) - \frac{\hbar^2}{24}\int dx \frac{n'(x)^2}{n(x)} + \ldots \;.$$

Wavy boxes

or $\hbar \longrightarrow 0$ or $v(x)$ flat.

Semiclassical density for 1d box

$$\boxed{n^{\mathrm{TF}}(x) = \frac{k_{\mathrm{F}}(x)}{\pi} - \frac{\sin 2\Theta_{\mathrm{F}}(x)}{2T_{\mathrm{F}}\, k_{\mathrm{F}}(x) \sin\alpha(x)}}$$

Classical momentum: $k(x) = \sqrt{2(\mathcal{E} - v(x))}$

Classical phase: $\Theta(x) = \int_0^x \mathrm{d}x'\; k(x')$

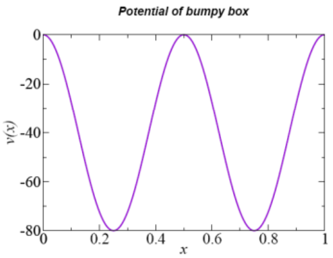
Fermi energy: $\Theta_F(L) = (N + \frac{1}{2})/\pi$

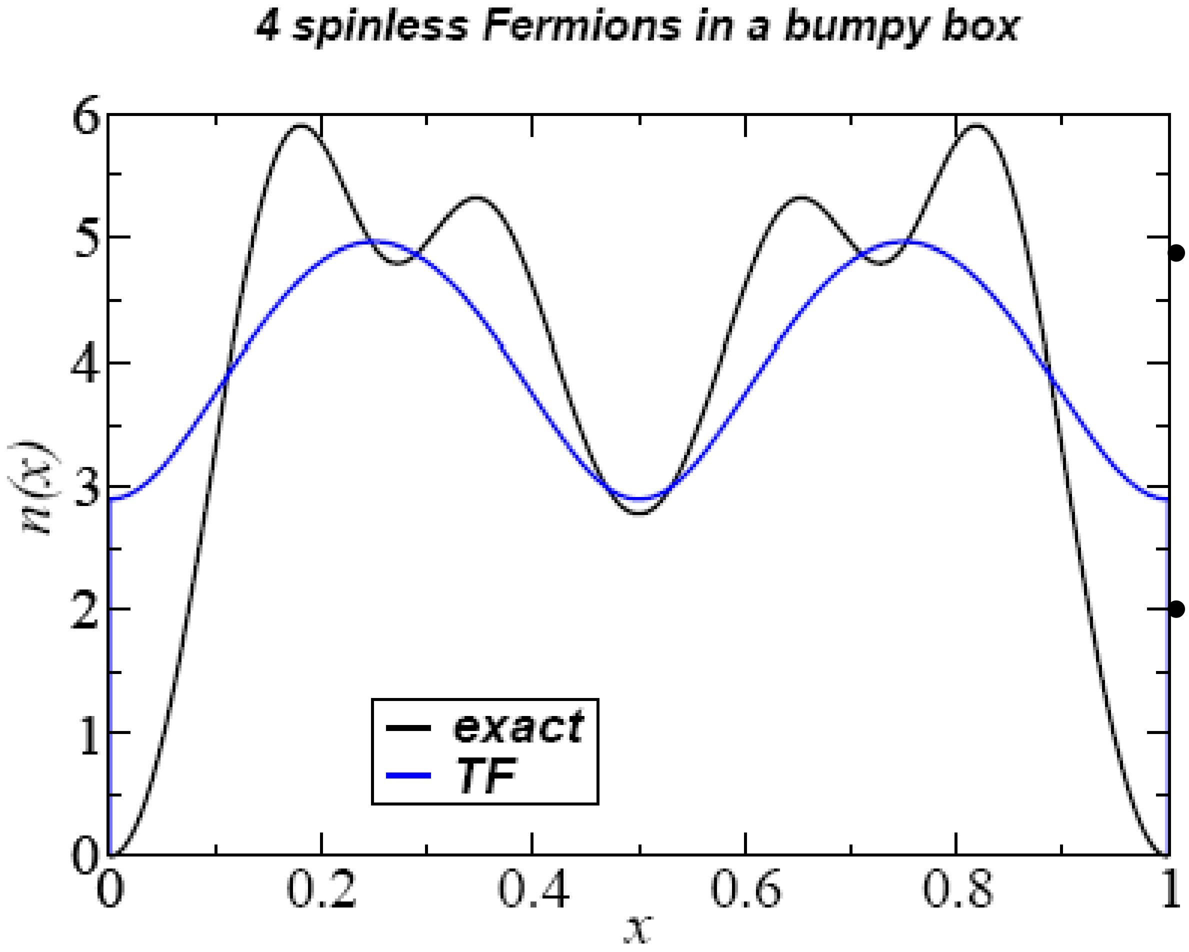
Classical transit time: $\tau_{\mathrm{F}}(x) = \int_0^x \mathrm{d}x'/k_{\mathrm{F}}(x')$

$$T_{\mathrm{F}} = \tau_{\mathrm{F}}(L) \qquad \alpha(x) = \pi\tau_{\mathrm{F}}(x)/T_{\mathrm{F}}$$

Elliott, Cangi, Lee, KB, PRL 2008

Density in bumpy box





- Exact density:
  - $T^{TF}[n]=153.0$
- Thomas-Fermi density:
  - $T^{TF}[n^{TF}]=115$
- Semiclassical density:
  - $T^{TF}[n^{semi}]=151.4$
  - $\Delta N < 0.2\%$

Usual continua

- Scattering states:
  - For a finite system, $E > 0$
- Solid-state: Thermodynamic limit
  - For a periodic potential, have continuum bands

A new continuum

- Consider some simple problem, e.g., harmonic oscillator.
- Find ground-state for one particle in well.
- Add a second particle in first excited state, but divide ħ by 2, and resulting density by 2.
- Add another in next state, and divide ħ by 3, and density by 3
- …
- →∞

Classical Continuum limit

Leading corrections to local approximations Attila Cangi, Donghyung Lee, Peter Elliott, and Kieron Burke, Phys. Rev. B 81, 235128 (2010).

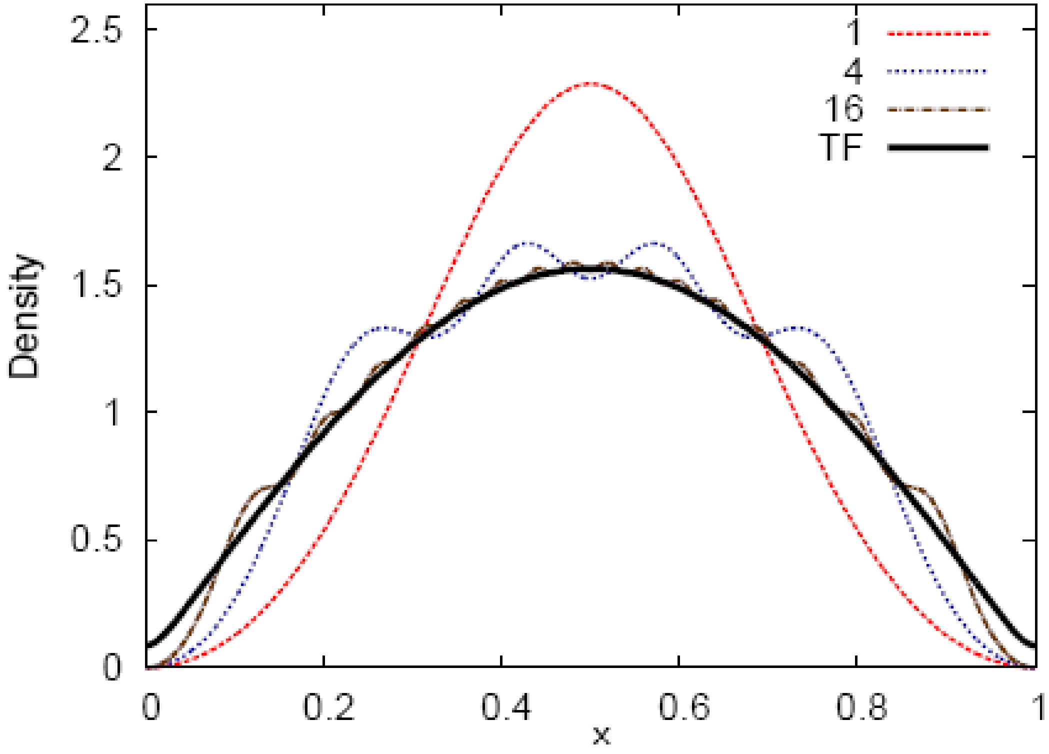
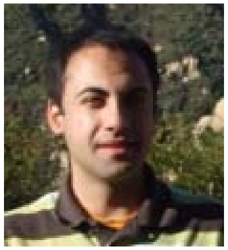


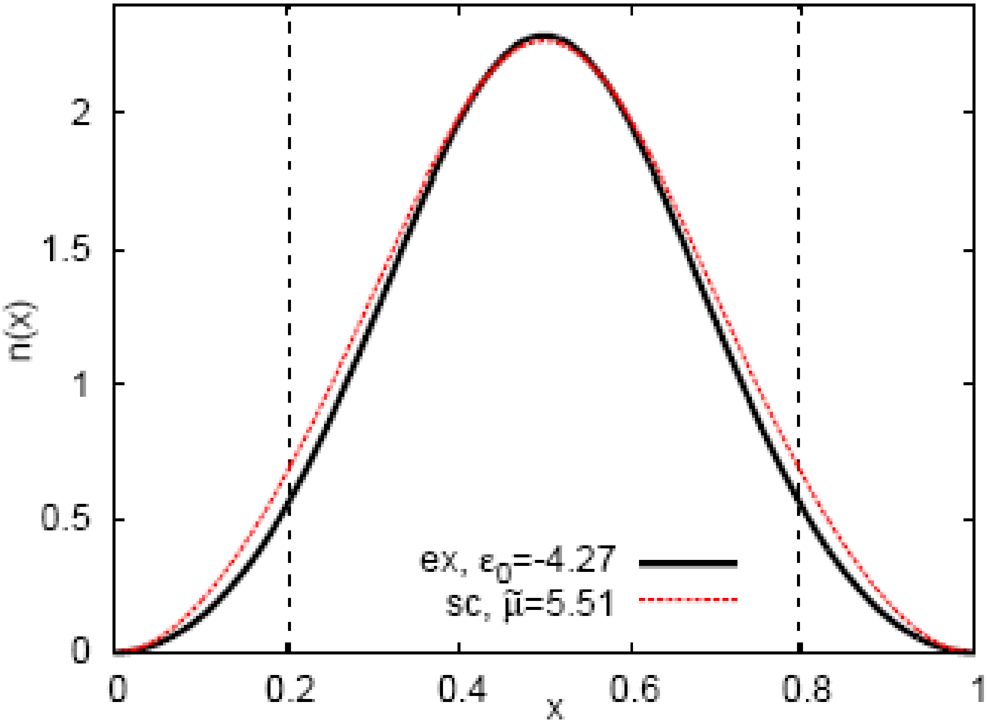
FIG. 2: TF and renormalized exact densities for $N' = 1, 4, \text{and} 16$ particles in $v(x) = -12\sin^2(\pi x), 0 \leq x \leq 1$, showing approach to continuum limit.



Attila Cangi

Example of utility of formulas

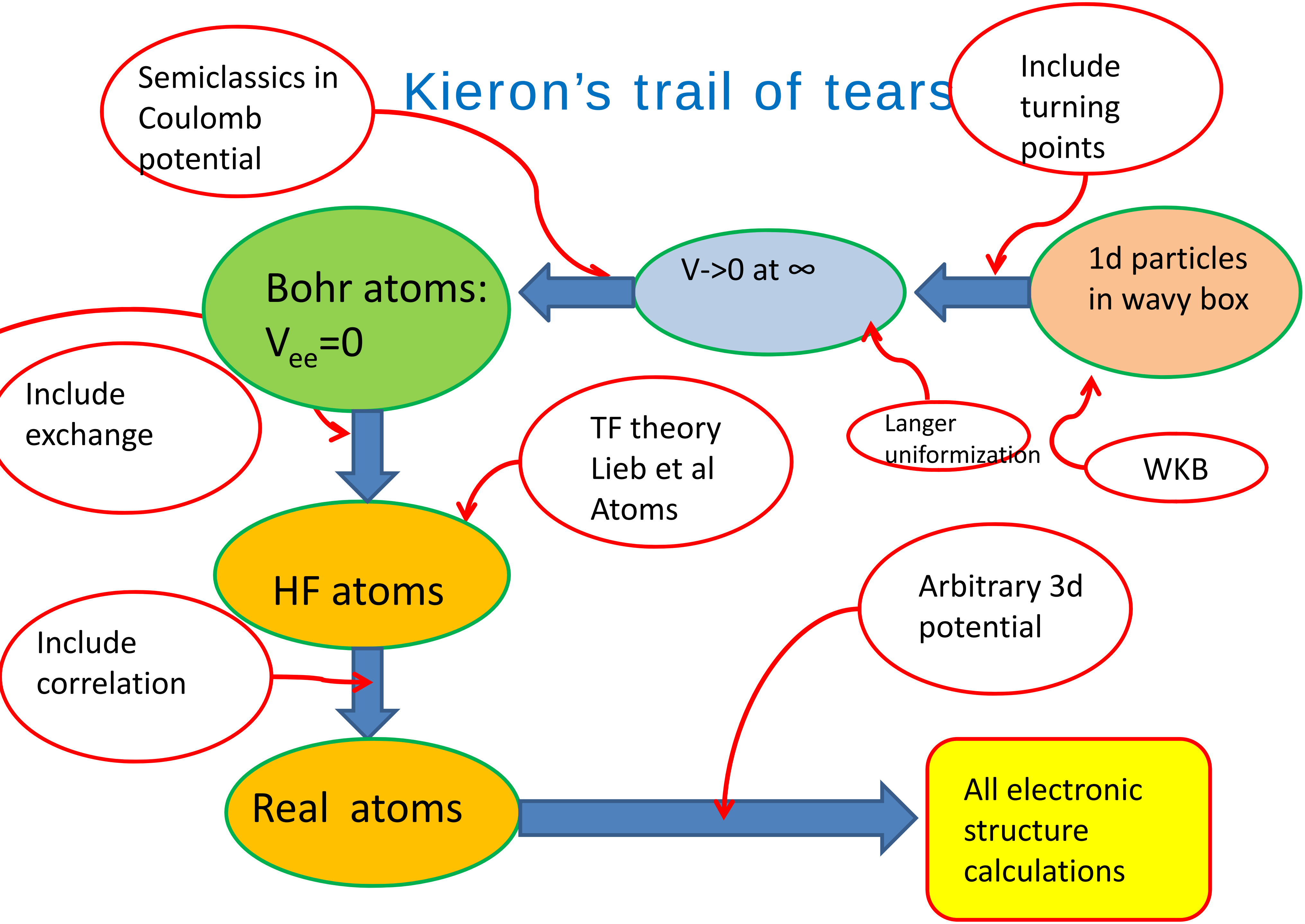
- Worst case (*N*=1)
- Note accuracy outside of turning points
- No evanescent contributions in formula



$$n^{\mathrm{semi}}(x) = \frac{k_{\mathrm{F}}(x)}{\pi} - \frac{\sin 2\Theta_{\mathrm{F}}(x)}{2T_{\mathrm{F}}\, k_{\mathrm{F}}(x) \sin\alpha(x)}$$

FIG. 9: Exact and approximate ground-state densities for $v(x) = -12\sin^2(\pi x)$, where $0 \le x \le 1$. The lowest eigenvalue is $\epsilon_0 = -6.64$ and $\tilde{\mu} = 4.26$. The position of the turning points is indicated by dashed lines.

Kieron’s trail of tears



Semiclassics in
Coulomb
potential

Include
turning
points

Bohr atoms:
V_{ee}=0

V->0 at ∞

1d particles
in wavy box

Include
exchange

TF theory
Lieb et al
Atoms

Langer
uniformization

WKB

HF atoms

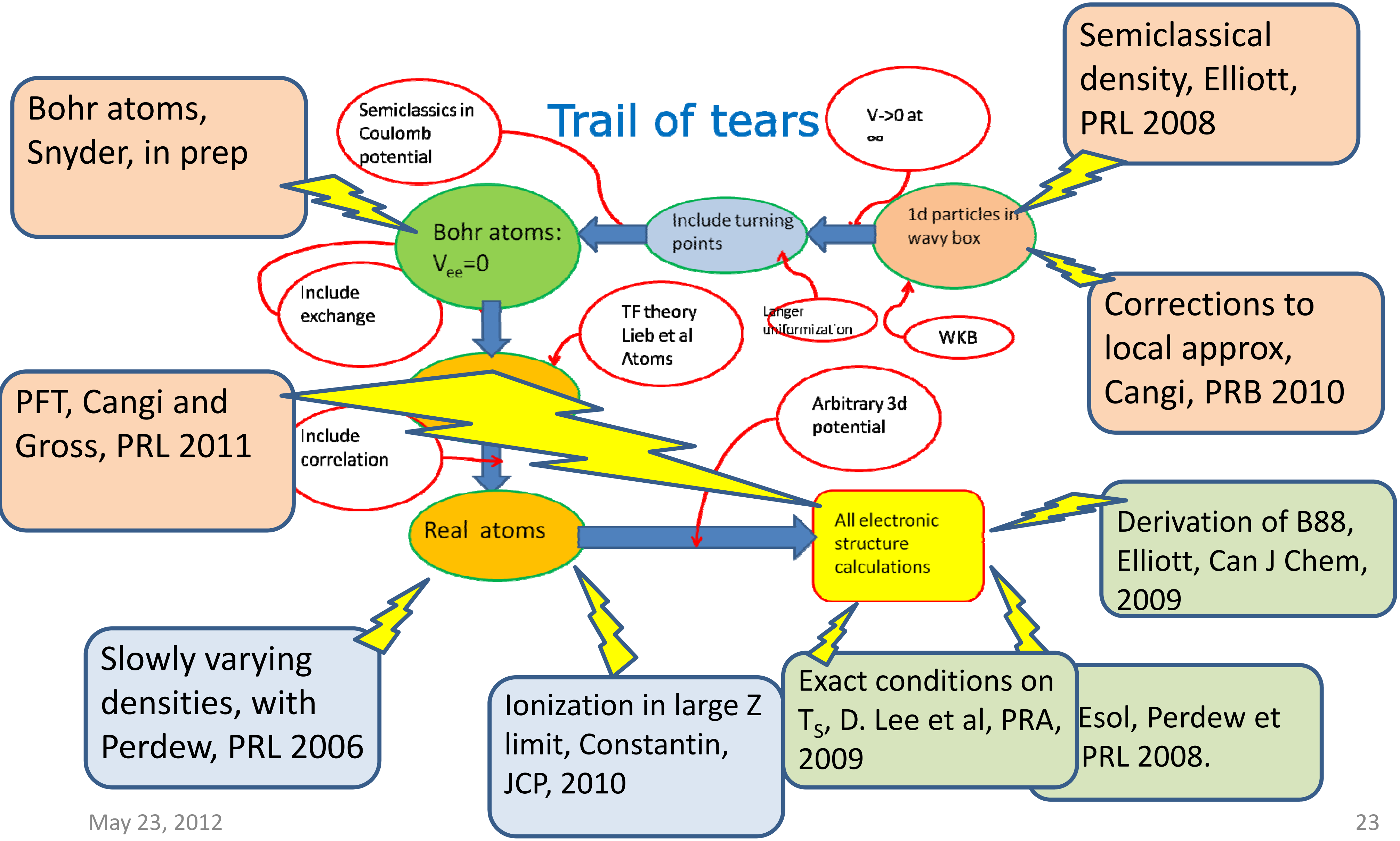
Arbitrary 3d
potential

Include
correlation

Real atoms

All electronic
structure
calculations

What we've done so far



Trail of tears

Semiclassics in Coulomb potential

V->0 at ∞

Bohr atoms: V_{ee}=0

Include turning points

1d particles in wavy box

Include exchange

TF theory Lieb et al Atoms

Langer uniformization

WKB

Include correlation

Arbitrary 3d potential

Real atoms

All electronic structure calculations

Bohr atoms, Snyder, in prep

Semiclassical density, Elliott, PRL 2008

Corrections to local approx, Cangi, PRB 2010

PFT, Cangi and Gross, PRL 2011

Derivation of B88, Elliott, Can J Chem, 2009

Slowly varying densities, with Perdew, PRL 2006

Ionization in large Z limit, Constantin, JCP, 2010

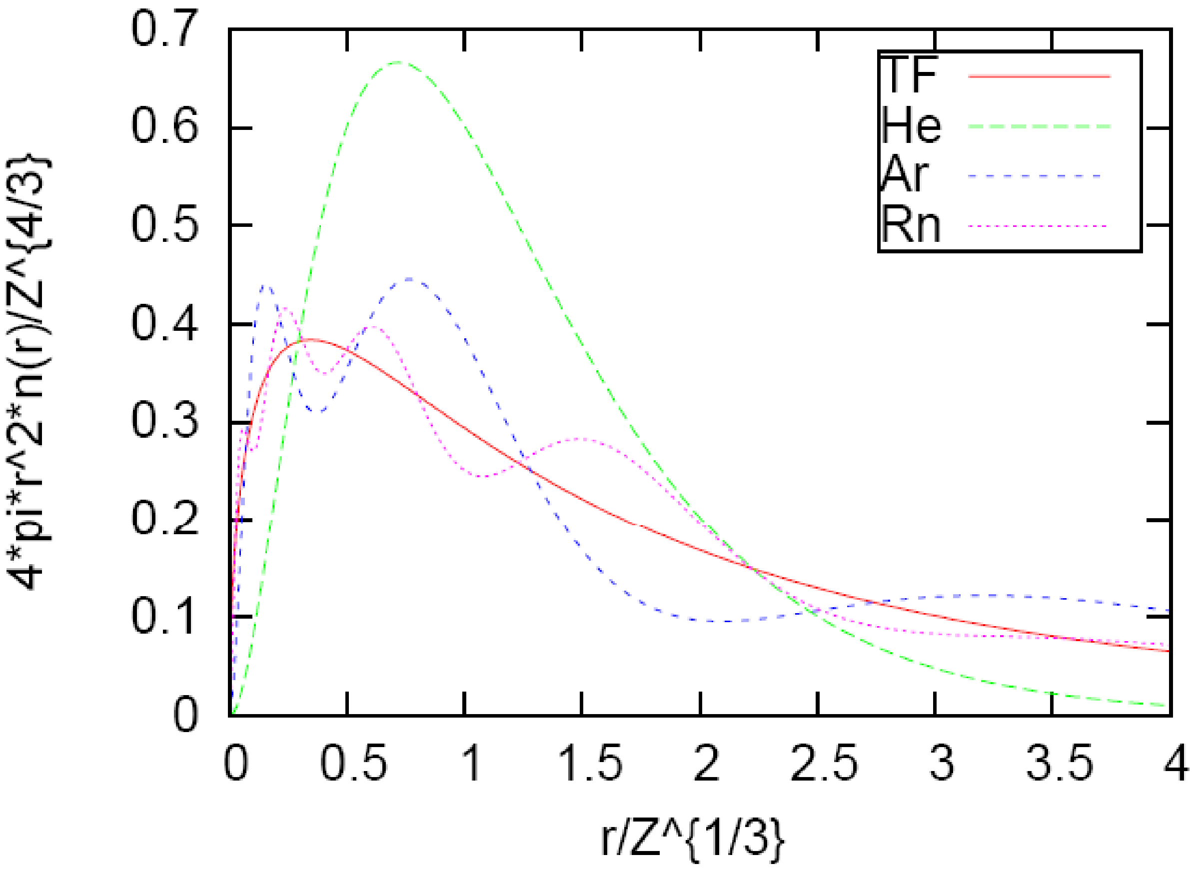
Exact conditions on T_S, D. Lee et al, PRA, 2009

Esol, Perdew et PRL 2008.

Back toward reality

Classical limit for neutral atoms

- For interacting systems in 3d, increasing *Z* in an atom, keeping it neutral, approaches the classical continuum, i.e. same as ħ→0
- Can study E_x as Z→∞, *find universal limit*

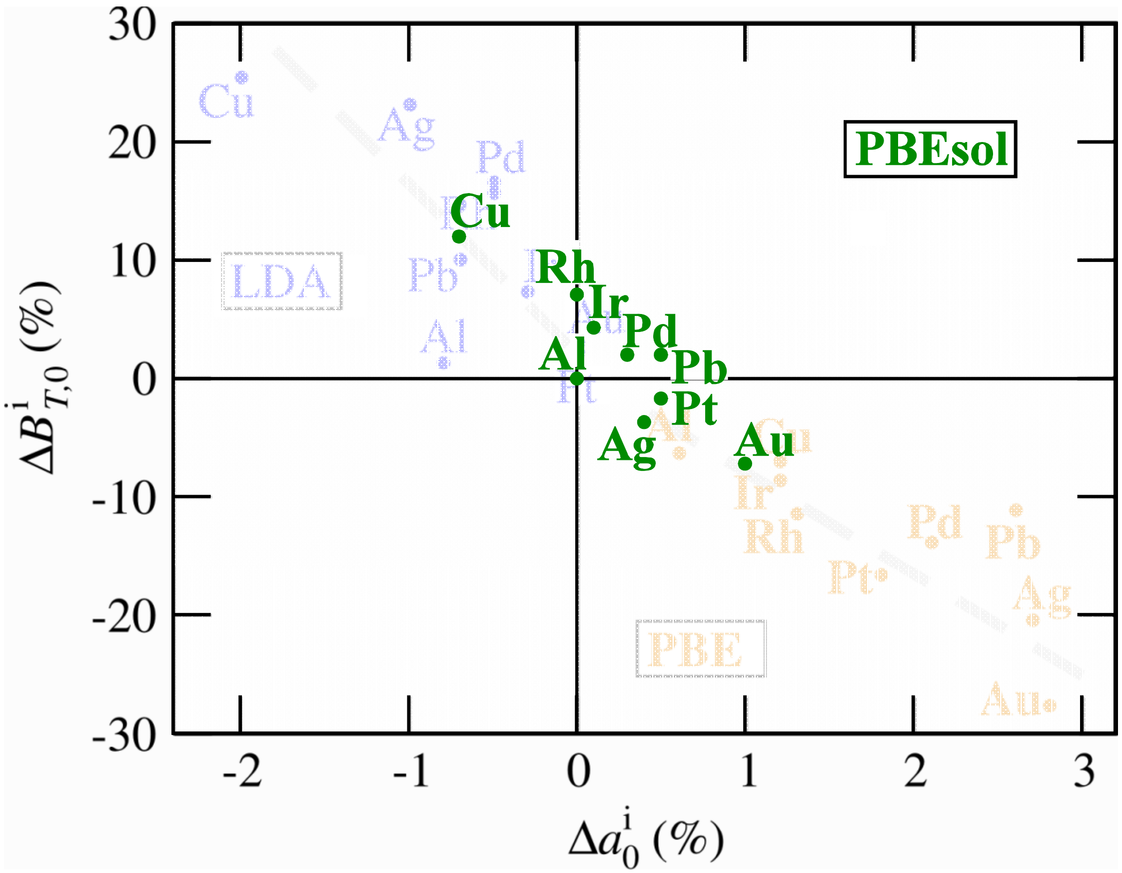


A major ultimate aim: $E_{XC}[n]$

- Explains why gradient expansion needed to be generalized (*Relevance of the slowly-varying electron gas to atoms, molecules, and solids* J. P. Perdew, L. A. Constantin, E. Sagvolden, and K. Burke, Phys. Rev. Lett. 97, 223002 (2006).)
- Derivation of β parameter in B88 (*Non-empirical 'derivation' of B88 exchange functional* P. Elliott and K. Burke, Can. J. Chem. 87, 1485 (2009).).
- PBEsol *Restoring the density-gradient expansion for exchange in solids and surfaces* J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008))
  - explains failure of PBE for lattice constants and fixes it at cost of good thermochemistry

Structural and Elastic Properties

Errors in LDA/GGA(PBE)-DFT computed lattice constants and bulk modulus with respect to experiment



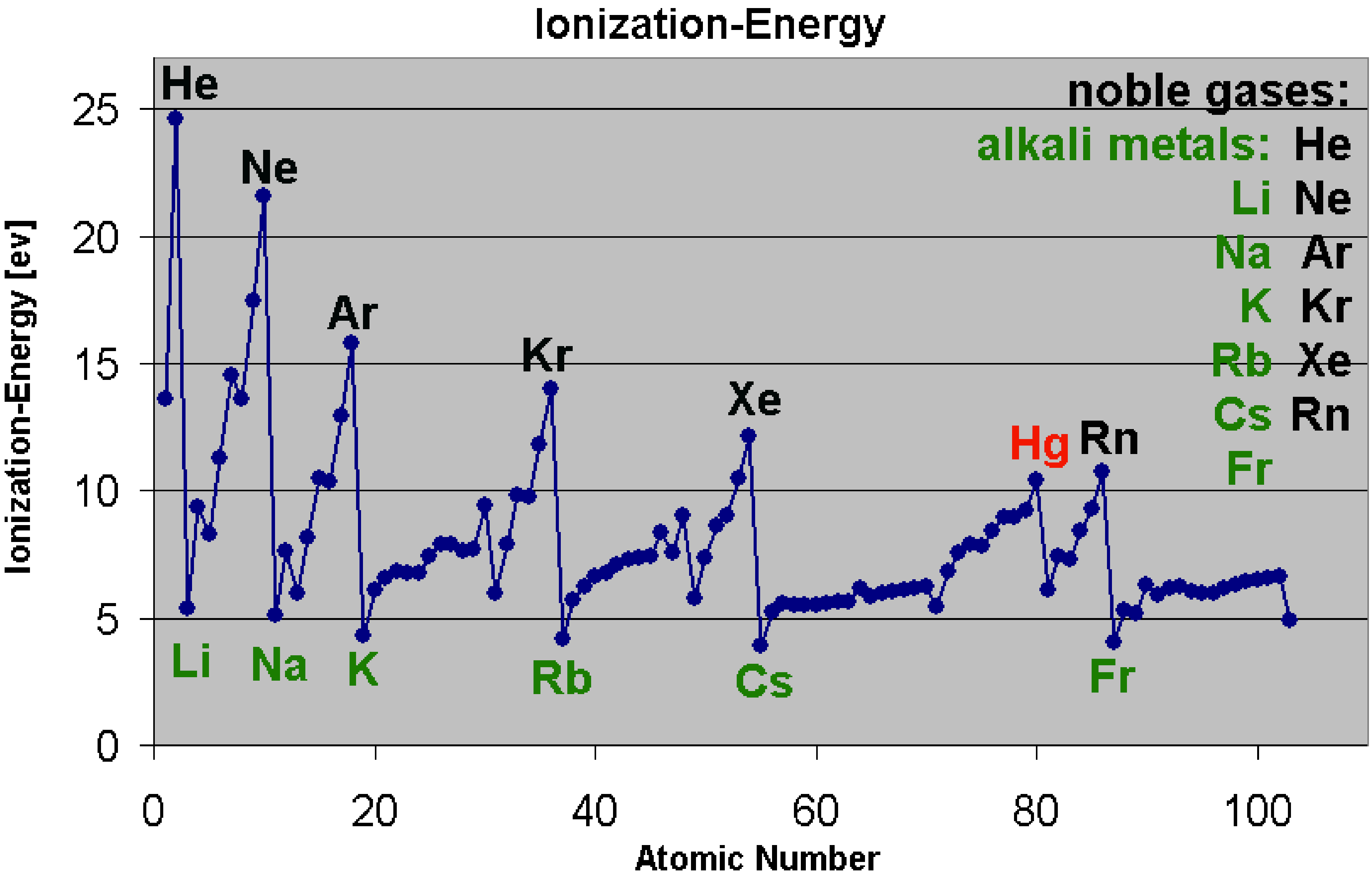
Blazej Grabowski, Dusseldorf

→ Fully converged results (basis set, k-sampling, supercell size)
→ Error solely due to xc-functional

→ GGA does not outperform LDA
→ characteristic errors of
  <3% in lat. const.
  < 30% in elastic const.
→ LDA and GGA provide bounds to exp. data
  → provide "ab initio error bars"

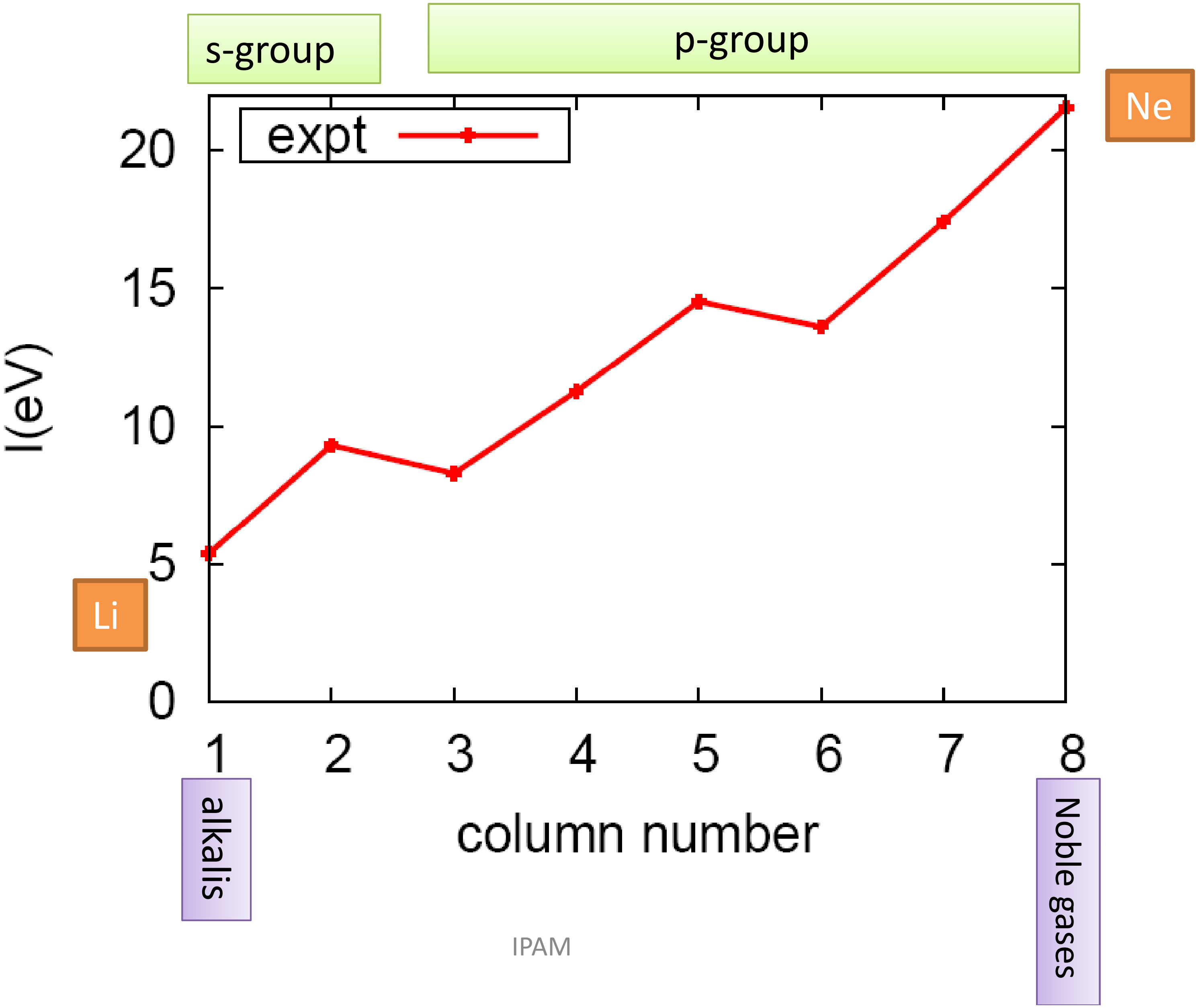
⇒ **Inspection of several xc-functionals is critical to estimate predictive power and error bars!**

What about energy differences?

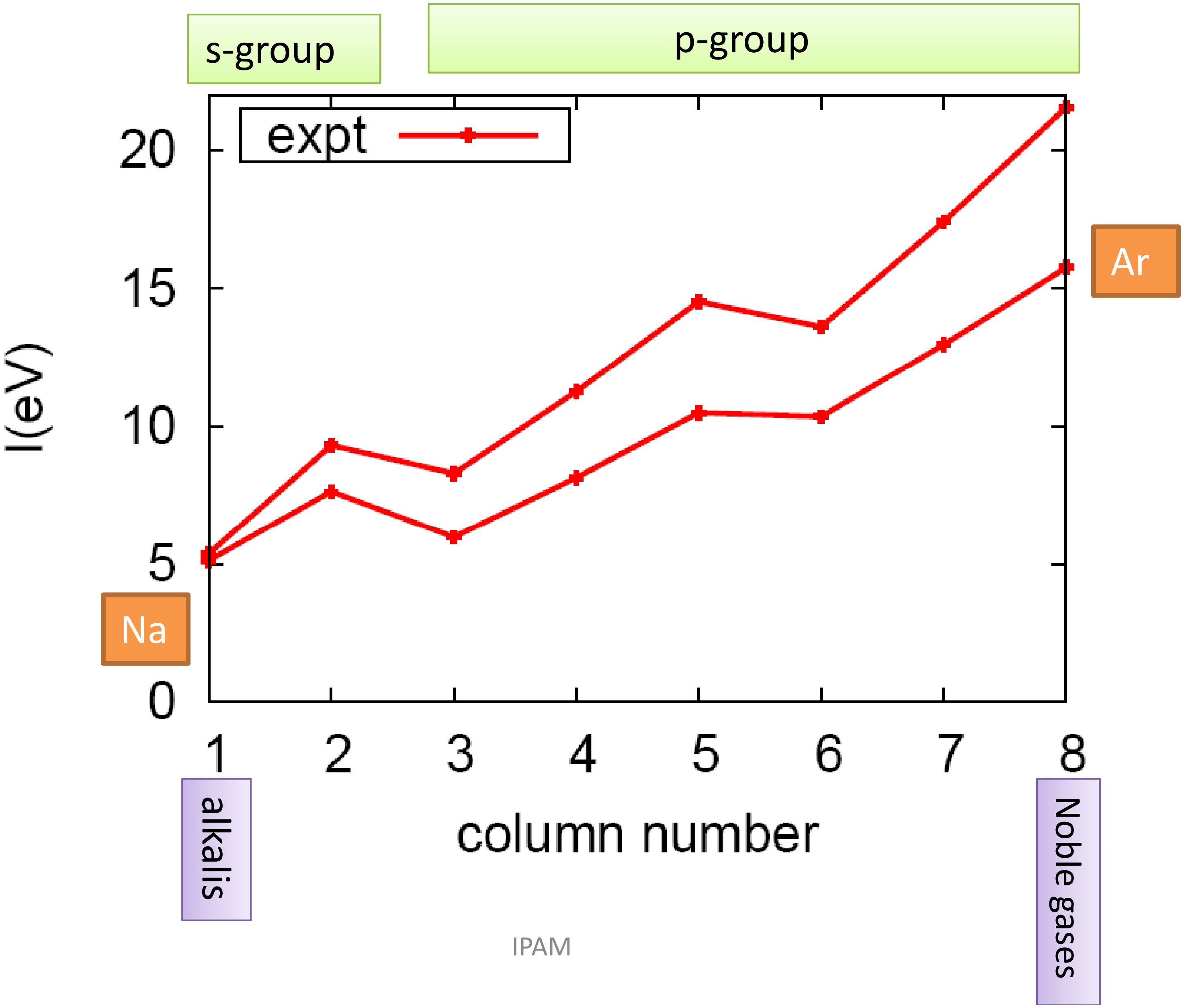


- wikipedia

I along first row



I along first and second rows



Ionization as Z→∞

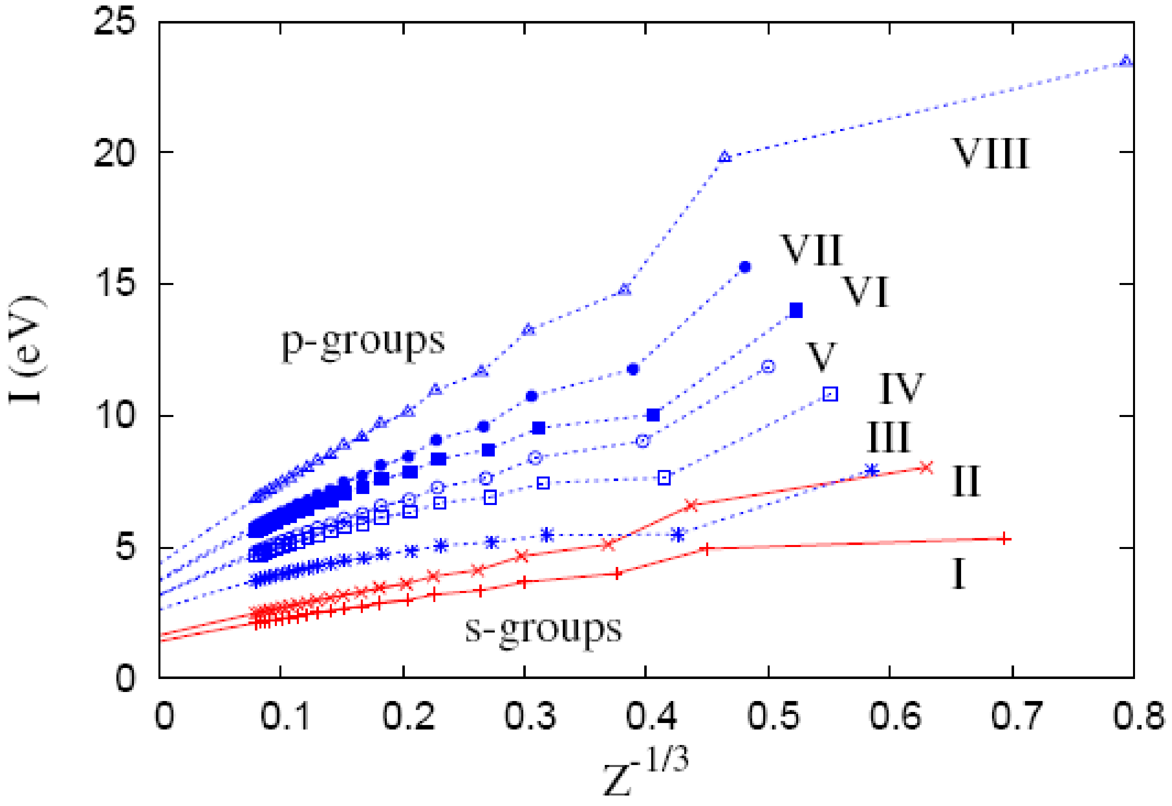
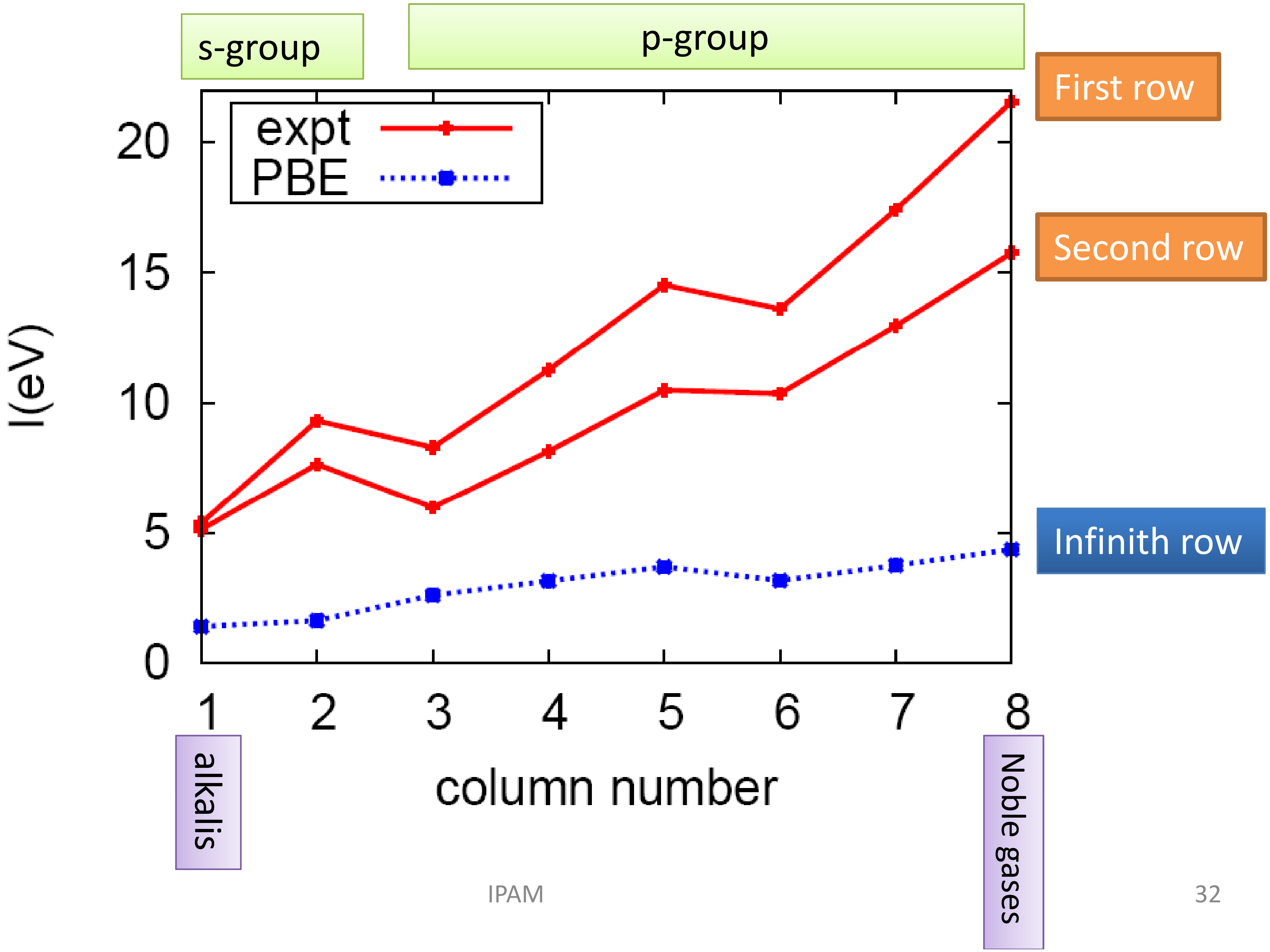


FIG. 2: OEP ionization potential I (in eV) versus $Z^{-1/3}$ for main groups of the periodic table.

Using code of Eberhard Engel, do HF for upto 3000 electrons

Lucian Constantin

I along last row



s-group

p-group

First row

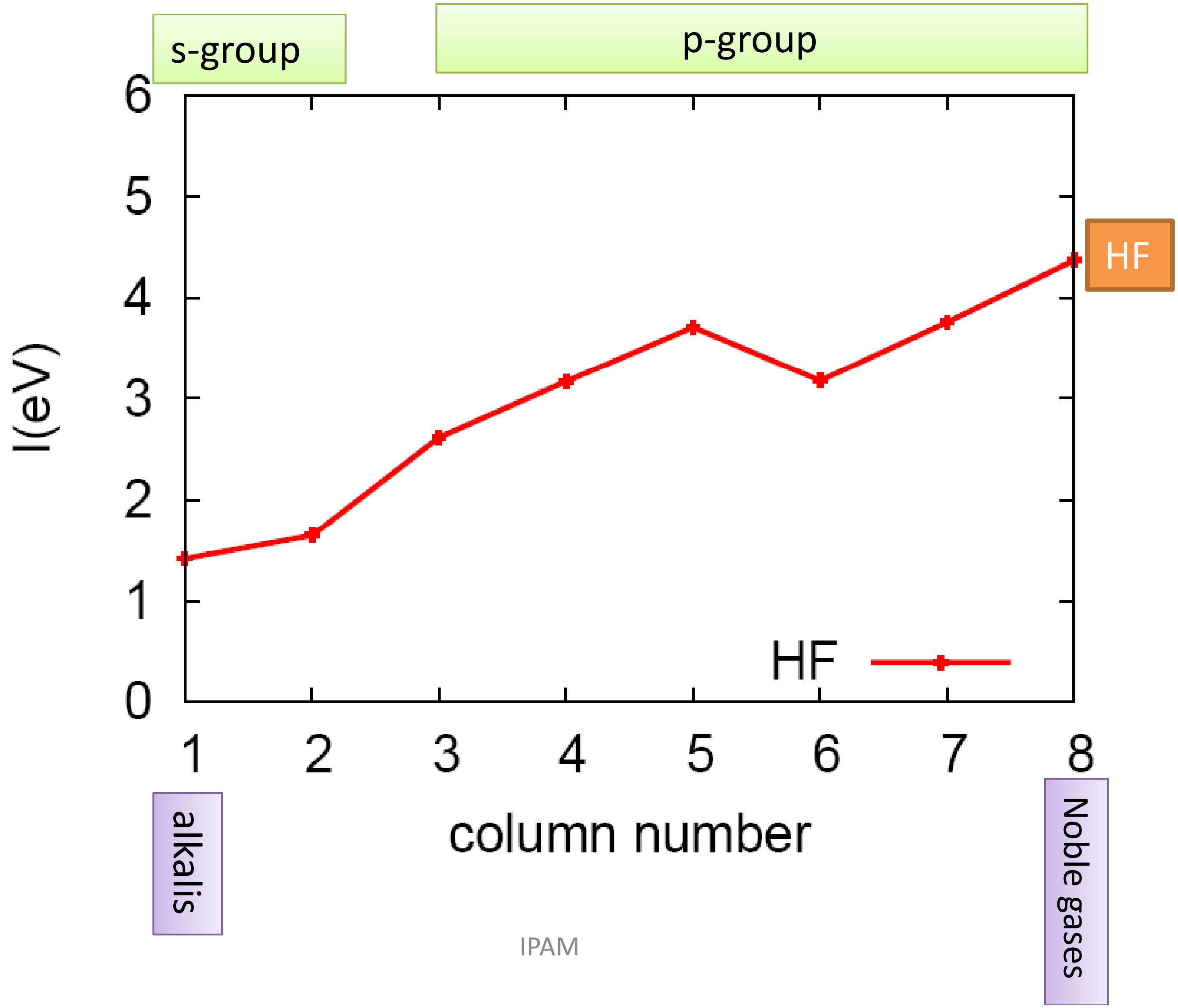
Second row

Infinith row

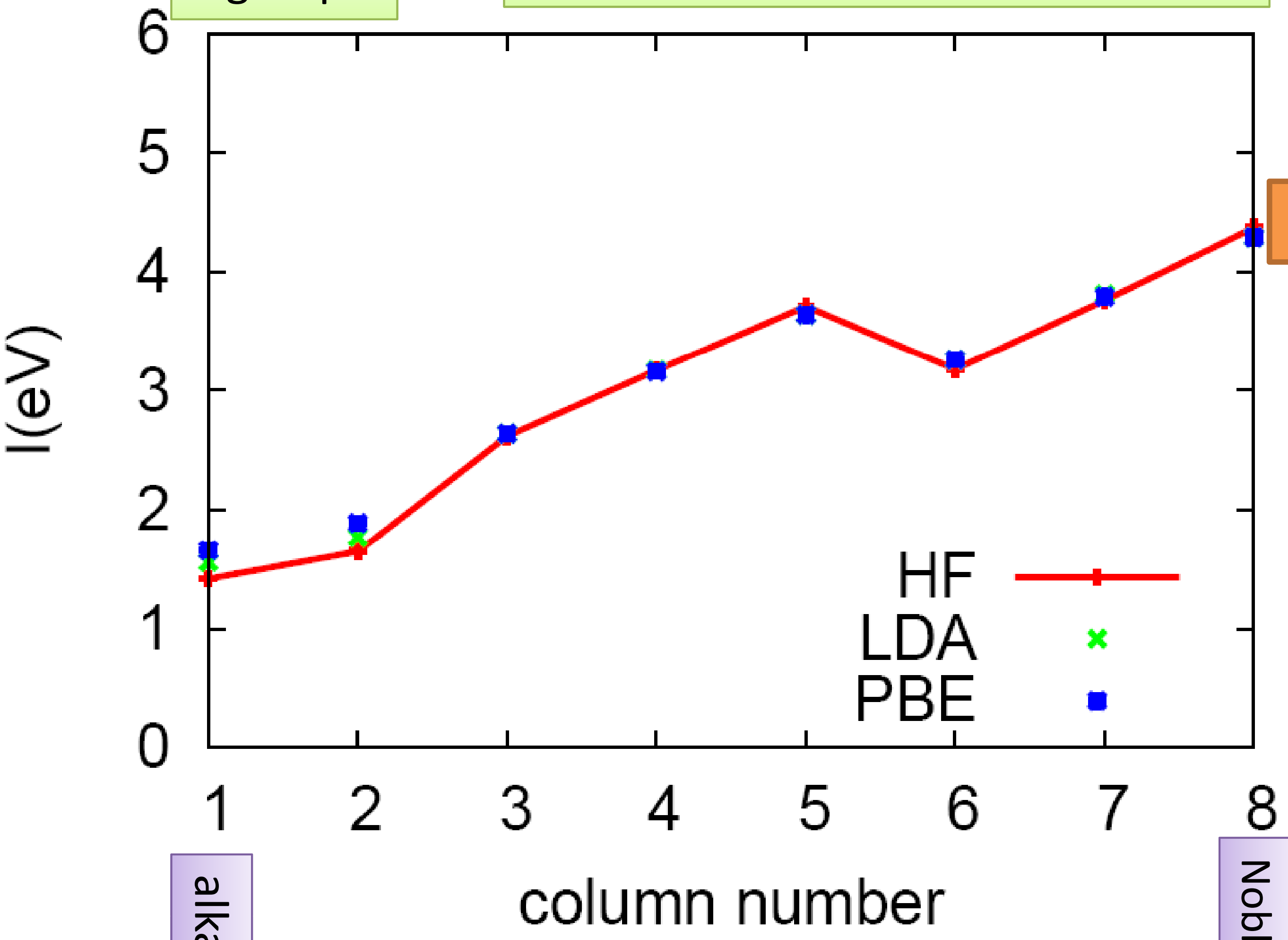
alkalis

Noble gases

I along last row



I along last row



s-group

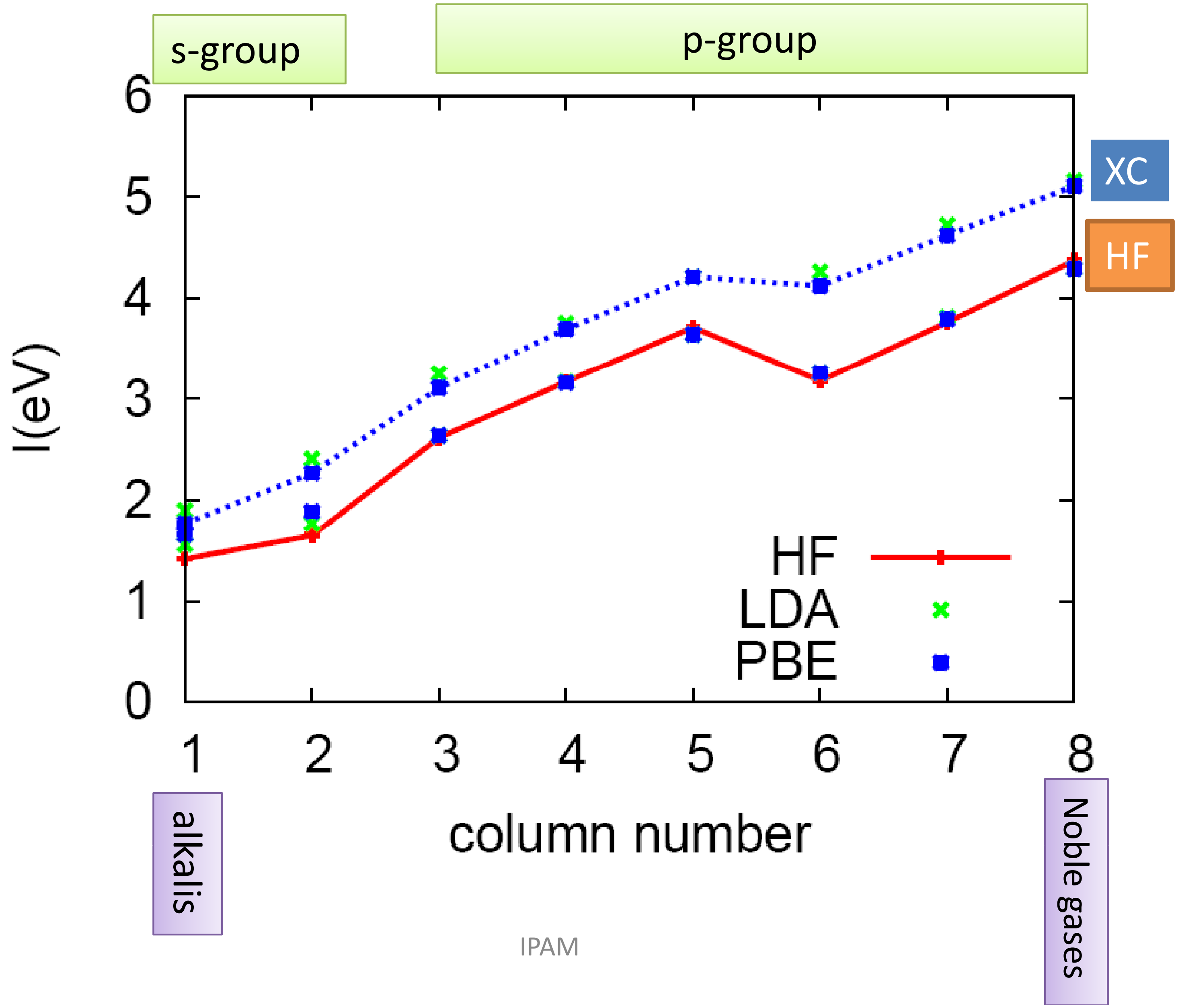
p-group

HF

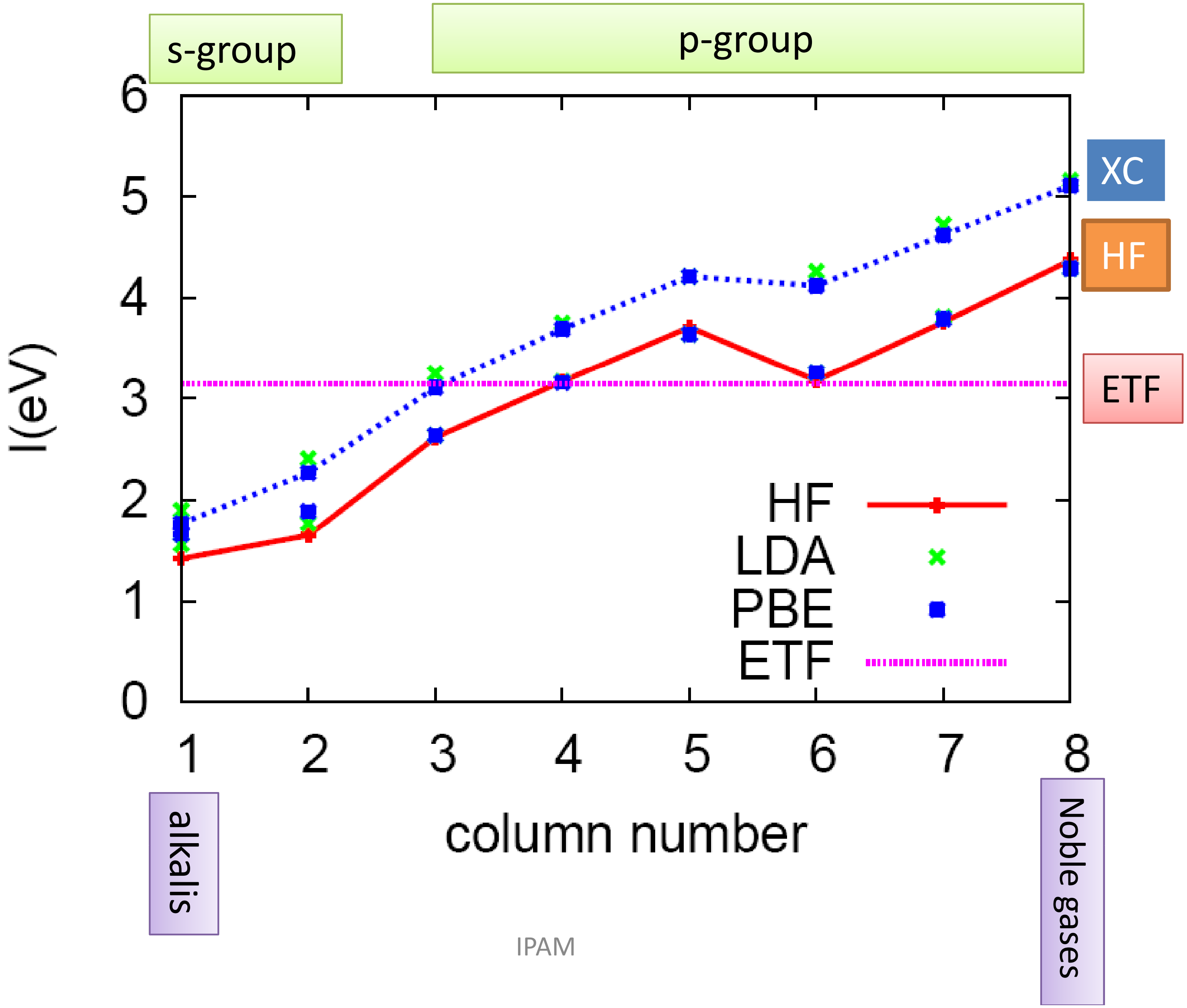
alkalis

Noble gases

I along last row



I along last row



Z→∞ limit of ionization potential

- Shows even energy differences can be found
- Looks like LDA exact for E_X as Z-> ∞.
- Looks like finite E_C corrections
- Looks like extended TF (treated as a potential functional) gives some sort of average.
- Lucian Constantin, John Snyder, JP Perdew, and KB, JCP (2010).

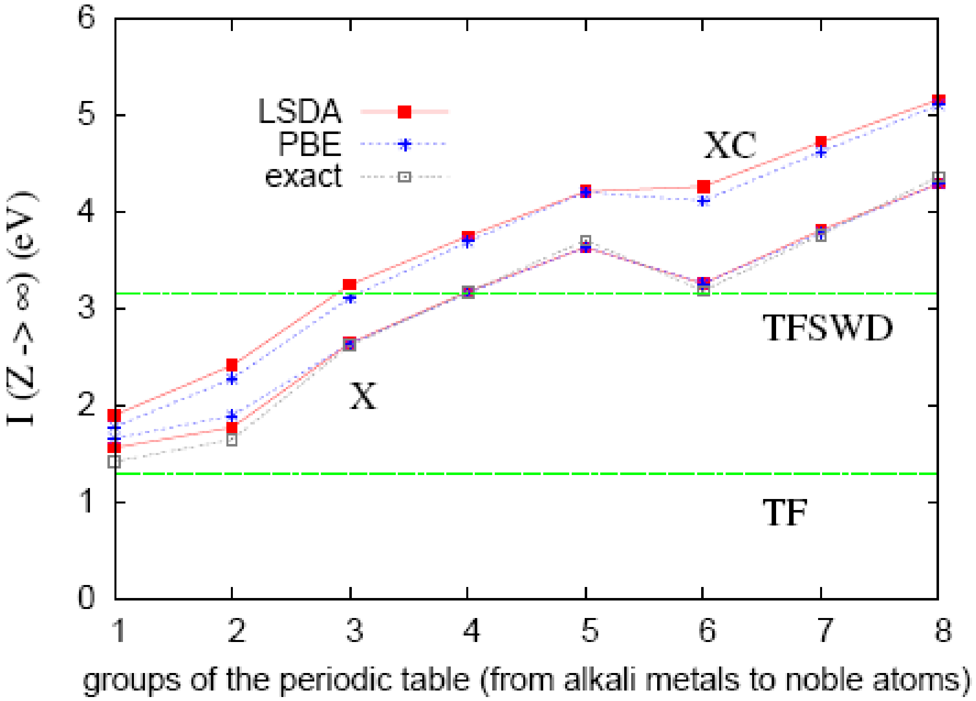


FIG. 1: Ionization potentials of the main groups in the limit of large row number of the periodic table, calculated using exact exchange, the local (spin) density approximation (LSD), and PBE. We also show the extended TF result.

Ionization density for large Z

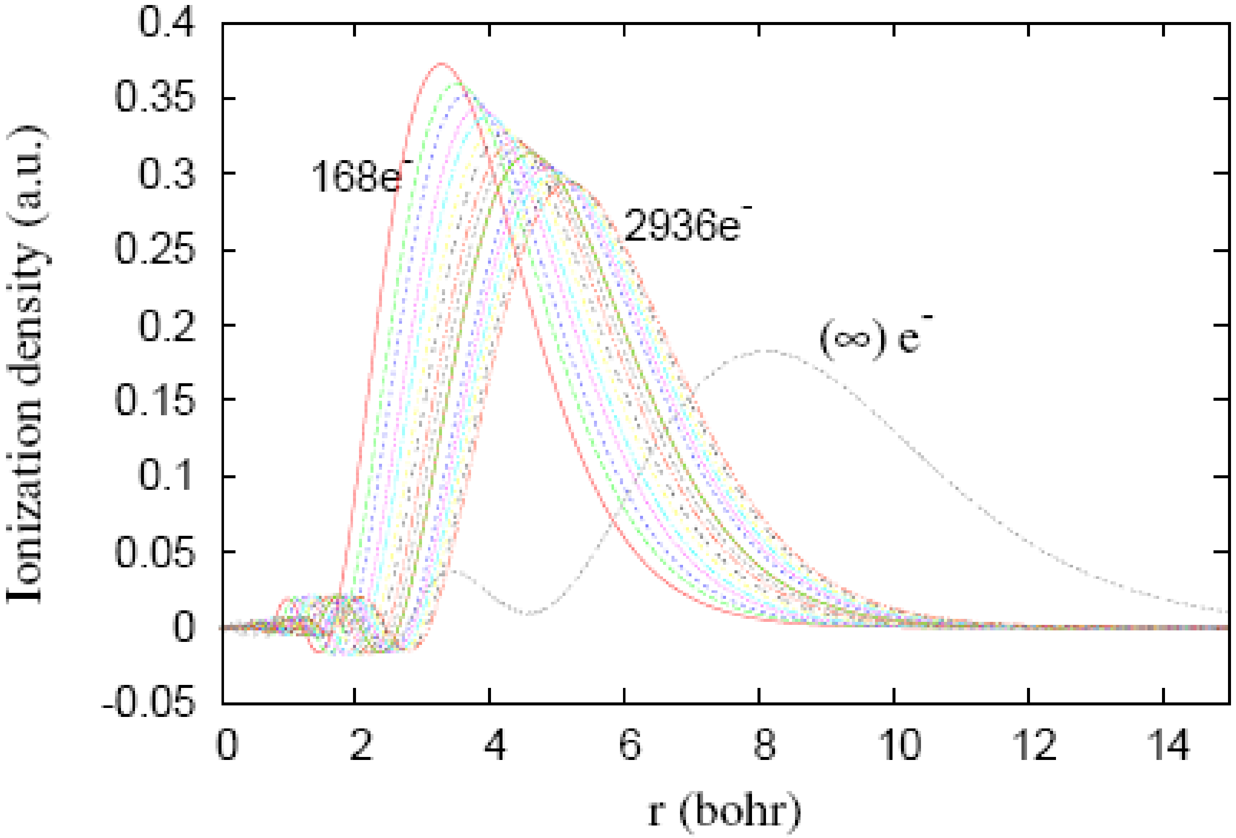
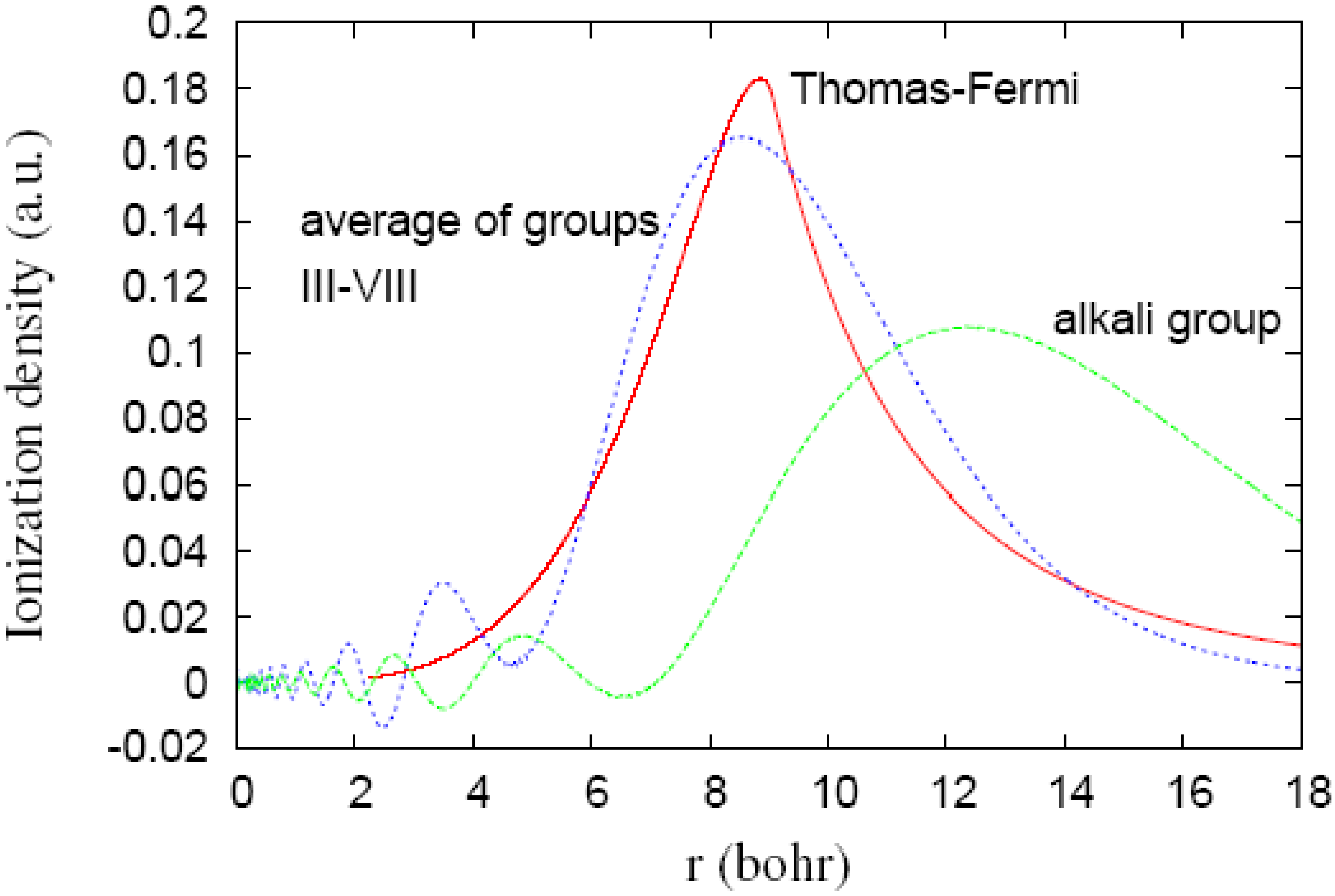


FIG. 4: Same as Fig. 3, but for the VIIIth or noble-gas column of the periodic table at various finite Z and in the limit $Z \to \infty$.

Ionization density as Z→∞



Potential functional approximations

A. **Cangi**, D. Lee, P. Elliott, KB, and E.K.U. Gross, **Phys. Rev. Lett. 106, 236404 (2011)**

$$F^{\rm cc}[v] = \int d^3r\, \{\bar{n}^{\rm A}[v](\mathbf{r}) - n^{\rm A}[v](\mathbf{r})\}\ v(\mathbf{r})$$

$$T_{\rm s}^{\rm cc}[n_{\rm s}^{\rm A}[v]] = \int d^3r\, \{\bar{n}_{\rm s}^{\rm A}[v](\mathbf{r}) - n_{\rm s}^{\rm A}[v](\mathbf{r})\}\ v(\mathbf{r})$$

$$v^\lambda(\mathbf{r}) = (1-\lambda)\, v_0(\mathbf{r}) + \lambda\, v(\mathbf{r})\ , \quad \bar{n}[v](\mathbf{r}) = \int_0^1 d\lambda\ n[v^\lambda](\mathbf{r})$$

- **Universal functional F** and **non-interacting kinetic energy** T_s as a functional of the **potential**.
- **No separate** approximation for T_s required.
- Conditions are derived under which potential-functional approximations are **variational**.
- Imposition of these conditions greatly **improves** the **accuracy** of T_s .

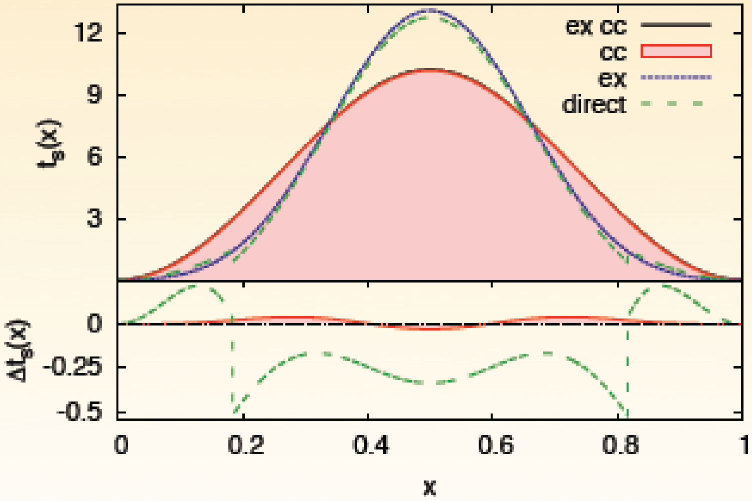


FIG. 1. Kinetic energy densities of $T_s^{\rm cc}$ (black, red) and the direct $T_s^{\rm A}$ (blue, green) of Ref. [18] (above), and their absolute errors (below) for one particle in $v(x) = -5\sin^2(\pi x)$, $0 < x < 1$. (color online)

New results in PFT

- Universal functional of v(**r**):

$$F[v] = \langle \Psi[v] | \hat{T} + \hat{V}_{\rm ee} | \Psi[v] \rangle$$

- Direct evaluation of energy:

$$E_v^{\rm A,dir} = F^{\rm A}[v] + \int d^3r \, n^{\rm A}[v](\mathbf{r}) \, v(\mathbf{r})$$

Coupling constant:

$$v^{\lambda}(\mathbf{r}) = (1-\lambda)\, v_0(\mathbf{r}) + \lambda\, v(\mathbf{r})$$

- New expression for F:

$$F[v] = \int d^3r\, \{\bar{n}[v](\mathbf{r}) - n[v](\mathbf{r})\}\; v(\mathbf{r})$$

Variational principle

$$E^{\mathrm{A,var}} = \min_{\tilde{v}} \left\{ F^{\mathrm{A}}[\tilde{v}] + \int d^3r\, n^{\mathrm{A}}[\tilde{v}](\mathbf{r})\, v(\mathbf{r}) \right\}$$

- Necessary and sufficient condition for same result:

$$\chi^{\mathrm{A}}[v](\mathbf{r},\mathbf{r}') = \delta n^{\mathrm{A}}[v](\mathbf{r})/\delta v(\mathbf{r}')$$

$$\chi^{\mathrm{A}}[v](\mathbf{r},\mathbf{r}') = \chi^{\mathrm{A}}[v](\mathbf{r}',\mathbf{r})$$

All you need is n[v](**r**)

- Any approximation for the non-interacting density as a functional of v(**r**) produces immediate self-consistent KS potential and density

$$v_{\mathrm{S}}(\mathbf{r}) = v(\mathbf{r}) + \int \mathrm{d}^3r' \, \frac{n[v_{\mathrm{S}}](\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\mathrm{XC}}[n[v_{\mathrm{S}}]](\mathbf{r})$$

Evaluating the energy

- With a pair $T_s^A[v]$ and $n_s^A[v](\mathbf{r})$, can get E two ways:

$$E_v^{\mathsf{A}} = T_{\mathsf{S}}^{\mathsf{A}}[v] + \int d^3r\, n_{\mathsf{S}}^{\mathsf{A}}[v](\mathbf{r})\, v(\mathbf{r})$$

$$E_v^{\mathsf{A}\prime} = \min_{\tilde{v}} \left\{ T_{\mathsf{S}}^{\mathsf{A}}[\tilde{v}] + \int d^3r\, n_{\mathsf{S}}^{\mathsf{A}}[\tilde{v}](\mathbf{r})\, v(\mathbf{r}) \right\}$$

- Both yield same answer if

$$\frac{\delta T_{\mathsf{S}}^{\mathsf{A}}[v]}{\delta v(\mathbf{r})} = -\int d^3r'\; v(\mathbf{r}')\, \frac{\delta n_{\mathsf{S}}^{\mathsf{A}}[v](\mathbf{r}')}{\delta v(\mathbf{r})} \;.$$

Coupling constant formula for energy

- Choose any reference (e.g., $v_0(\mathbf{r})=0$) and write

$$v^\lambda(\mathbf{r}) = (1-\lambda)\, v_0(\mathbf{r}) + \lambda\, v(\mathbf{r})\,;$$

- Do usual Pauli trick

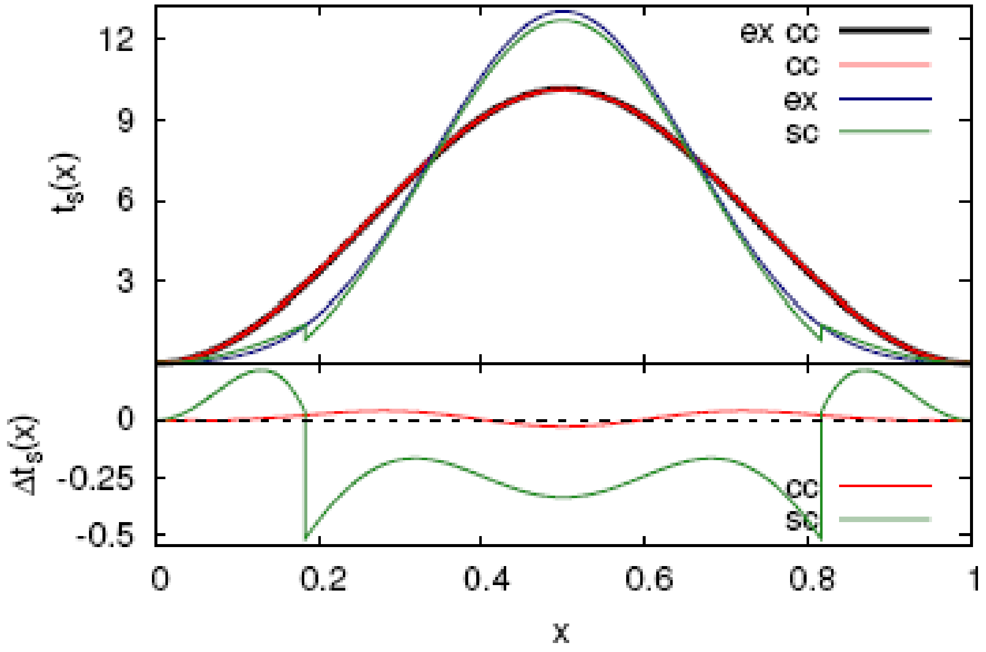
$$E_v = E_0 + \int_0^1 d\lambda \int d^3r \; n[v^\lambda](\mathbf{r})\, \Delta v(\mathbf{r})$$

- Yields $T_s[v]$ directly from $n[v]$:

$$T_{\mathsf{S}}^{\mathsf{cc}}[v] = \int d^3r \; \{\bar{n}_{\mathsf{S}}^{\mathsf{A}}[v](\mathbf{r}) - n_{\mathsf{S}}^{\mathsf{A}}[v](\mathbf{r})\}\; v(\mathbf{r})$$

Different kinetic energy density

- CC formula gives DIFFERENT kinetic energy density (from any usual definitions)
- But approximation much more accurate globally and point-wise than with direct approximation

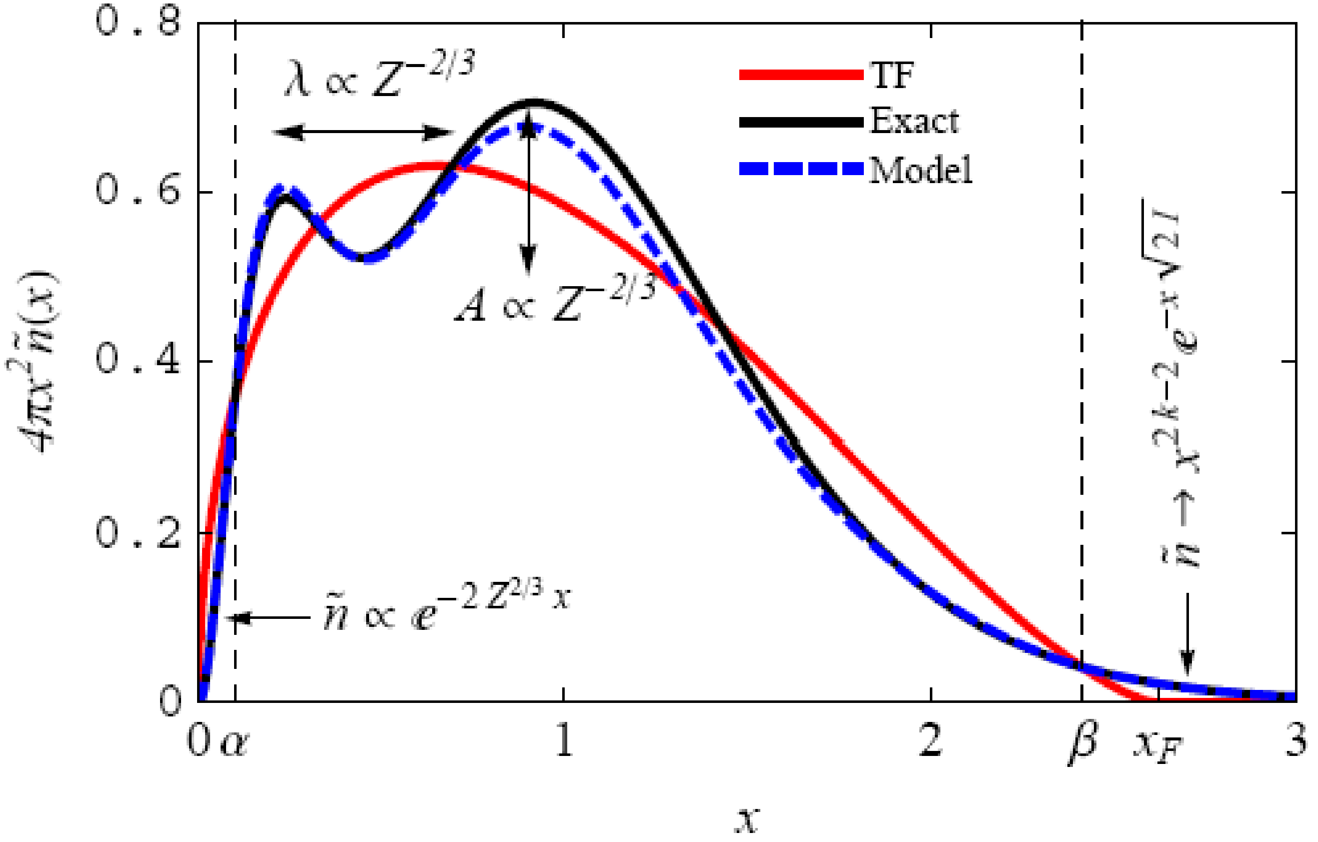


Getting to real systems

- Include real turning points and evanescent regions, using Langer uniformization
- Consider spherical systems with Coulombic potentials (Langer modification)
- Develop methodology to numerically calculate corrections for arbitrary 3d arrangements

Bohr atom

- Atoms with e-e repulsion made infinitesimal

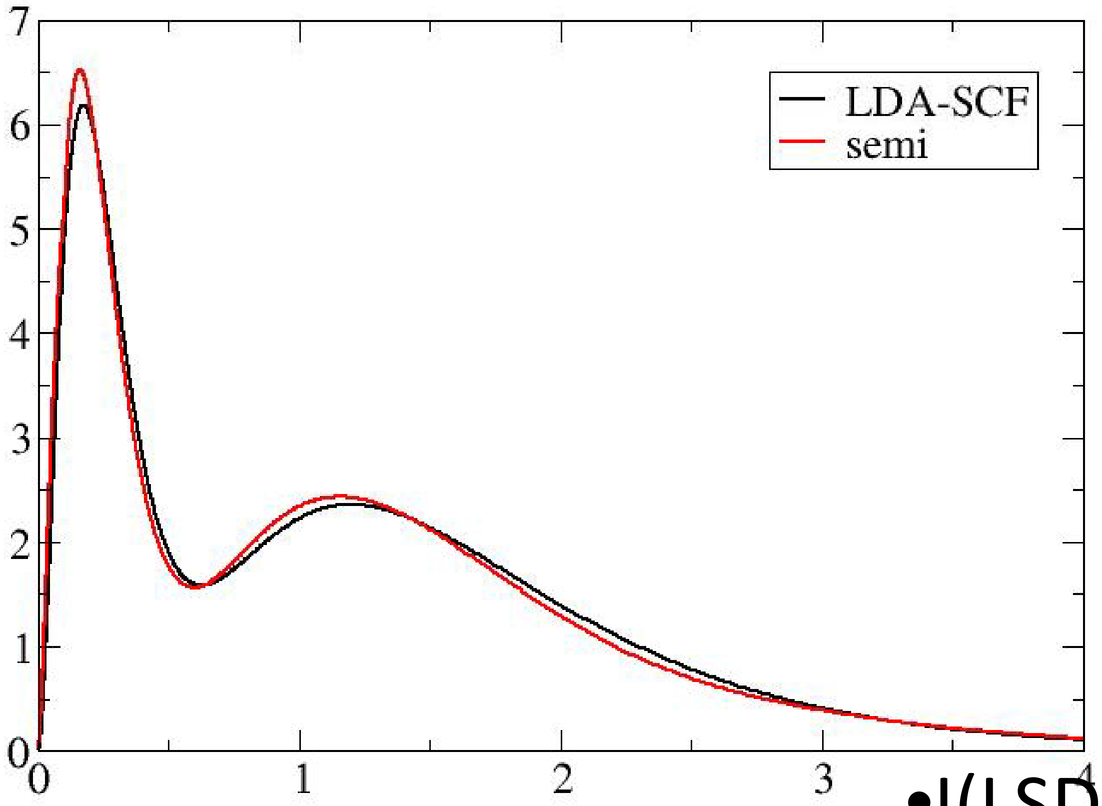


$x=Z^{1/3}r$,

$Z=28$

Orbital-free potential-functional for C density (Dongyung Lee)

$4\pi r^2 n(r)$



r

- I(LSD)=11.67eV
- I(PFT)=11.43 eV
- I(expt)=11.26eV

Essential question

- When do local approximations become relatively exact for a quantum system?
- What is nature of expansion?
- What are leading corrections?

Need help

- Asymptotic analysis
- Semiclassical theory, including periodic orbits
- Boundary layer theory
- Path integrals
- Green’s functions for many-body problems
- Random matrix theory

Conclusions

- All work in progress – Rome was not burnt in a day
- For E_{XC}:
  - Already have bits and pieces
  - Beginning assault on $E_X[n]$
- For T_S:
  - Strongly suggests orbital-free calculations should use potential not density
  - Now have improved formula for getting T directly from any n[v](r)
  - Developing path-integral formulation
- Thanks to students, collaborators, and NSF