Density-Functional Theory and Chemistry in One Dimension

Pierre-François Loos

Research School of Chemistry,
Australian National University,
Canberra, Australia

14ème Rencontre des Chimistes Théoriciens Francophones,
École Nationale Supérieure de Chimie de Paris

July 2nd 2014

Quantum Chemistry at ANU

Peter Gill
Q-Chem president

Andrew Gilbert
IQmol

Caleb Ball
DFT

Giuseppe Barca
HF excited states

Australian Government
Australian Research Council

Discovery Early Career Researcher Award 2013 + Discovery Project 2014

The local-density approximation (LDA)

The local-density approximation (LDA)

- Find the correlation energy of the **infinite** uniform electron gas (UEG) for all densities ρ
  Ceperley & Alder, Phys Rev Lett 45 (1980) 566

The local-density approximation (LDA)

- Find the correlation energy of the **infinite** uniform electron gas (UEG) for all densities ρ
  Ceperley & Alder, Phys Rev Lett 45 (1980) 566

- Treat a molecular density as a collection of tiny bits of UEG
  Vosko, Wilk & Nusair, Can J Phys 58 (1980) 1200
  Perdew & Zunger, Phys Rev B 23 (1981) 5048
  Perdew & Wang, Phys Rev B 45 (1992) 13244

The local-density approximation (LDA)

- Find the correlation energy of the **infinite** uniform electron gas (UEG) for all densities ρ
  Ceperley & Alder, Phys Rev Lett 45 (1980) 566

- Treat a molecular density as a collection of tiny bits of UEG
  Vosko, Wilk & Nusair, Can J Phys 58 (1980) 1200
  Perdew & Zunger, Phys Rev B 23 (1981) 5048
  Perdew & Wang, Phys Rev B 45 (1992) 13244

- ☺ The LDA is an *ab initio* model with no adjustable parameters
- ☺ This is an attractive approach to molecular electronic structure
- ☺ It also forms a foundation for more accurate approximations

The local-density approximation (LDA)

- Find the correlation energy of the **infinite** uniform electron gas (UEG) for all densities ρ
  Ceperley & Alder, Phys Rev Lett 45 (1980) 566

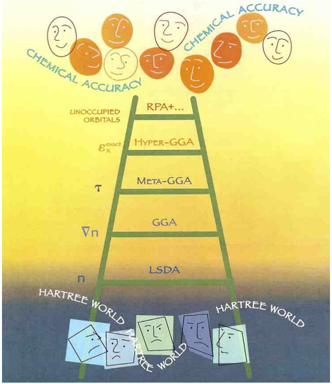
- Treat a molecular density as a collection of tiny bits of UEG
  Vosko, Wilk & Nusair, Can J Phys 58 (1980) 1200
  Perdew & Zunger, Phys Rev B 23 (1981) 5048
  Perdew & Wang, Phys Rev B 45 (1992) 13244

☺ The LDA is an *ab initio* model with no adjustable parameters
☺ This is an attractive approach to molecular electronic structure
☺ It also forms a foundation for more accurate approximations

☹☹ Not very accurate for correlation energy (overestimated by roughly 100%)

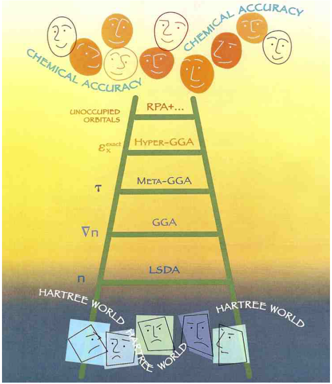
Jacob's ladder vs Generalized LDA idea

- The lowest rung (LDA) assumes that all UEGs of density ρ are equivalent



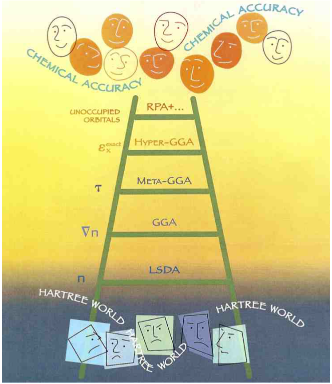
Jacob's ladder vs Generalized LDA idea

- The lowest rung (LDA) assumes that all UEGs of density ρ are equivalent
- That assumption is not correct!
  Gill & Loos, Theor Chem Acc 131 (2012) 1069
  Loos & Gill, J Chem Phys 138 (2013) 164124



Jacob's ladder vs Generalized LDA idea

- The lowest rung (LDA) assumes that all UEGs of density ρ are equivalent
- That assumption is not correct!
  Gill & Loos, Theor Chem Acc 131 (2012) 1069
  Loos & Gill, J Chem Phys 138 (2013) 164124
- We propose to follow an alternative route to heaven using finite-size UEGs!

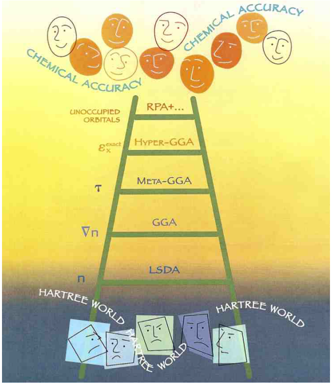


Jacob's ladder vs Generalized LDA idea

- The lowest rung (LDA) assumes that all UEGs of density ρ are equivalent
- That assumption is not correct!
  Gill & Loos, Theor Chem Acc 131 (2012) 1069
  Loos & Gill, J Chem Phys 138 (2013) 164124
- We propose to follow an alternative route to heaven using finite-size UEGs!
- We add a new local two-electron parameter

$$\text{hole curvature: } \eta(\mathbf{r}) \propto 2\sum_{i}^{\text{occ}} |\nabla\psi_i|^2 - \frac{|\nabla\rho|^2}{2\rho}$$

Loos, Ball & Gill, J Chem Phys 140 (2014) 18A524



GLDA correlation functional for 1D systems

$$E_{\text{c}}^{\text{GLDA}}(\rho,\eta) = \Upsilon_0(\eta)\, F\left[1, \frac{3}{2}, \Upsilon(\eta), \frac{\Upsilon_0(\eta)(1-\Upsilon(\eta))}{\Upsilon_\infty(\eta)}\, \rho^{-1}\right]$$

GLDA correlation functional for 1D systems

$$E_c^{\text{GLDA}}(\rho,\eta) = \Upsilon_0(\eta)\, F\left[1, \frac{3}{2}, \Upsilon(\eta), \frac{\Upsilon_0(\eta)(1-\Upsilon(\eta))}{\Upsilon_\infty(\eta)}\,\rho^{-1}\right]$$

$F(a,b,c,x)$	$=$	Hypergeometric function	$\Leftrightarrow$	exact for small and large ρ
$\Upsilon_0(\eta)$	$=$	electrons are close to each other	$\Leftrightarrow$	perturbation theory
$\Upsilon(\eta)$	$=$	intermediate densities	$\Leftrightarrow$	quantum Monte Carlo
$\Upsilon_\infty(\eta)$	$=$	electrons are far apart	$\Leftrightarrow$	perturbation theory

GLDA correlation functional for 1D systems

$$E_c^{\text{GLDA}}(\rho,\eta) = \Upsilon_0(\eta)\, F\left[1, \frac{3}{2}, \Upsilon(\eta), \frac{\Upsilon_0(\eta)(1-\Upsilon(\eta))}{\Upsilon_\infty(\eta)}\,\rho^{-1}\right]$$

$F(a,b,c,x)$	$=$	Hypergeometric function	$\Leftrightarrow$	exact for small and large ρ
$\Upsilon_0(\eta)$	$=$	electrons are close to each other	$\Leftrightarrow$	perturbation theory
$\Upsilon(\eta)$	$=$	intermediate densities	$\Leftrightarrow$	quantum Monte Carlo
$\Upsilon_\infty(\eta)$	$=$	electrons are far apart	$\Leftrightarrow$	perturbation theory

By construction, $E_c^{\text{GLDA}}(\rho,\eta=1) = E_c^{\text{LDA}}(\rho)$

GLDA correlation functional for 1D systems

$$E_c^{\text{GLDA}}(\rho,\eta) = \Upsilon_0(\eta)\, F\left[1, \frac{3}{2}, \Upsilon(\eta), \frac{\Upsilon_0(\eta)(1-\Upsilon(\eta))}{\Upsilon_\infty(\eta)}\, \rho^{-1}\right]$$

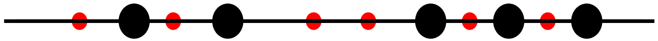
$F(a,b,c,x)$	=	Hypergeometric function	$\Leftrightarrow$	exact for small and large ρ
$\Upsilon_0(\eta)$	=	electrons are close to each other	$\Leftrightarrow$	perturbation theory
$\Upsilon(\eta)$	=	intermediate densities	$\Leftrightarrow$	quantum Monte Carlo
$\Upsilon_\infty(\eta)$	=	electrons are far apart	$\Leftrightarrow$	perturbation theory

By construction, $E_c^{\text{GLDA}}(\rho,\eta=1) = E_c^{\text{LDA}}(\rho)$

	Electrons in a box ($L=\pi$)					Electrons in a harmonic well ($k=1$)				
	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
LDA	46	73	99	126	154	42	66	90	115	139
GLDA	11	27	45	65	86	13	29	46	65	84
FCI	10	26	46	68	92	14	32	52	74	101

Loos, Phys Rev A 89 (2014) 052523

Chemistry in 1D with the Coulomb operator $|x|^{-1}$



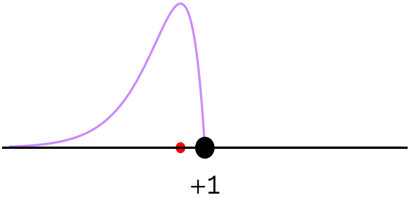
Loos, Ball & Gill (submitted)

Impenetrability of the 1D Coulomb potential: H atom

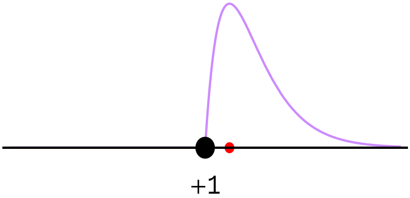
Newton, J Phys A 27 (1994) 4717; Nunez-Yepez et al., Phys Rev A 83 (2011) 064101.

Hydrogen atom in 1D

Left-handed ground state: $_1\mathbf{H}$



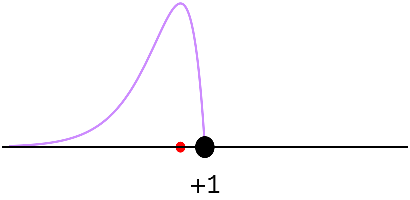
Right-handed ground state: $\mathbf{H}_1$



Loudon, Am J Phys 27 (1959) 649

Hydrogen atom in 1D

Left-handed ground state: $_1\mathbf{H}$

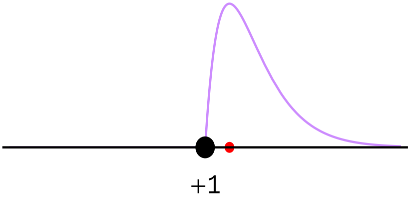


$$\psi(x) = -x \exp(+x)$$

$$E = -0.5$$

$$\mu = +1.5 \qquad R = \sqrt{\langle x^2 \rangle} = 1.8$$

Right-handed ground state: $\mathbf{H}_1$



$$\psi(x) = x \exp(-x)$$

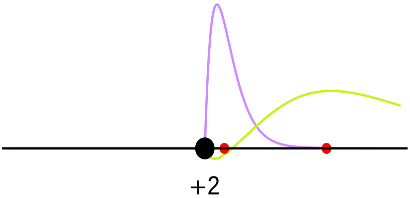
$$E = -0.5$$

$$\mu = -1.5 \qquad R = \sqrt{\langle x^2 \rangle} = 1.8$$

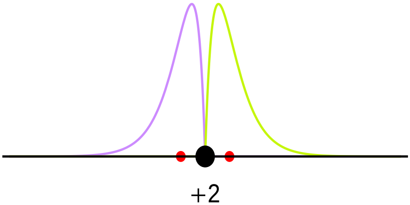
Loudon, Am J Phys 27 (1959) 649

Helium atom in 1D

One-sided helium: **$He_{1,2}$**

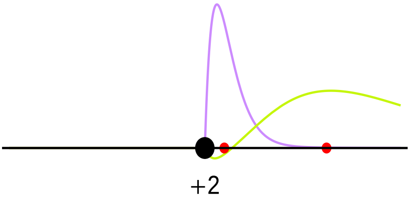


Two-sided helium: **${}_1He_1$**



Helium atom in 1D

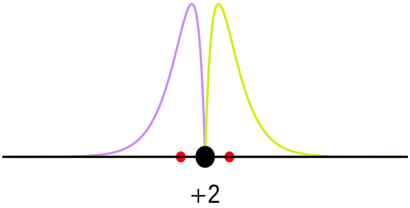
One-sided helium: $\mathbf{He}_{1,2}$



$E = -2.1074$

$\mu = +3.5 \qquad R = 4.8$

Two-sided helium: $_{1}\mathbf{He}_{1}$

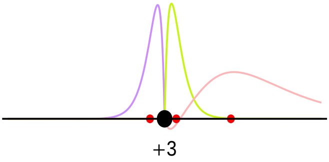


$E = -3.2429$

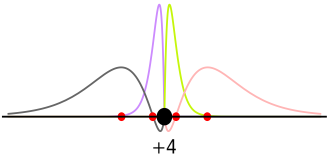
$\mu = 0 \qquad R = 1.0$

More 1D atoms...

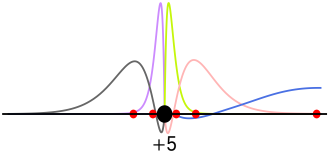
Lithium: $\mu = 1.5$ **and** $R = 2.8$



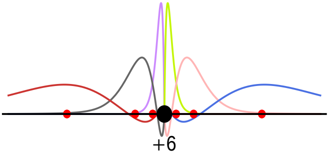
Beryllium: $\mu = 0$ **and** $R = 2.1$



Boron: $\mu = 1.9$ **and** $R = 4.7$



Carbon: $\mu = 0$ **and** $R = 3.7$



The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

- Odd electron ⇒ reactive

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron $\Rightarrow$ unfilled shell
- Even electron $\Rightarrow$ filled shell

- Odd electron $\Rightarrow$ reactive
- Even electron $\Rightarrow$ unreactive

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

- Odd electron ⇒ reactive
- Even electron ⇒ unreactive

- Odd electron ⇒ "alkali metals"

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

- Odd electron ⇒ reactive
- Even electron ⇒ unreactive

- Odd electron ⇒ "alkali metals"
- Even electron ⇒ "noble gases"

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

- Odd electron ⇒ reactive
- Even electron ⇒ unreactive

- Odd electron ⇒ "alkali metals"
- Even electron ⇒ "noble gases"

The periodic table in a 1D world...

Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron ⇒ unfilled shell
- Even electron ⇒ filled shell

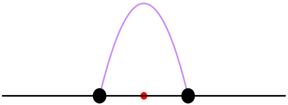
- Odd electron ⇒ reactive
- Even electron ⇒ unreactive

- Odd electron ⇒ "alkali metals"
- Even electron ⇒ "noble gases"

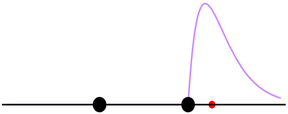
Group	1	2
	Alkali metals	Noble Gases
Period 1	1 H	2 He
2	3 Li	4 Be
3	5 B	6 C
4	7 N	8 O
5	9 F	10 Ne

The H_2^+ molecule in 1D

The H_1H^+ state: $\mu = 0$

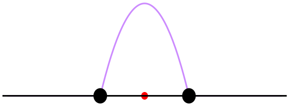


The $HH_1{}^+$ state: $\mu \neq 0$

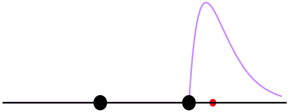


The H_2^+ molecule in 1D

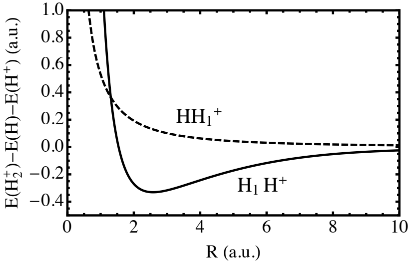
The H_1H^+ state: $\mu = 0$



The $HH_1{}^+$ state: $\mu \neq 0$

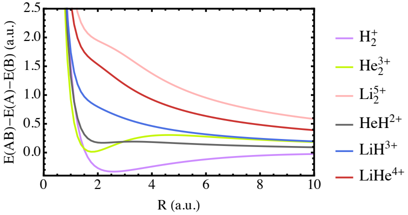


Potential energy curves for H_2^+

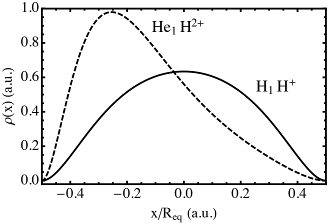


One-electron diatomic molecules in 1D

Potential energy curves for H_2^+-like molecules

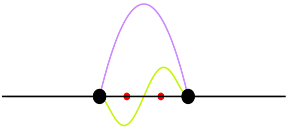


Electron densities for one-electron diatomics

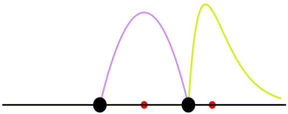


The H_2 molecule in 1D

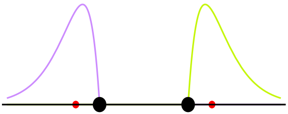
The $H_{1,2}H$ state



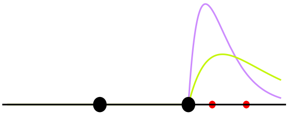
The H_1H_1 state



The ${}_1HH_1$ state

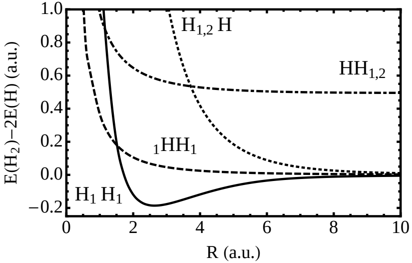


The $HH_{1,2}$ state

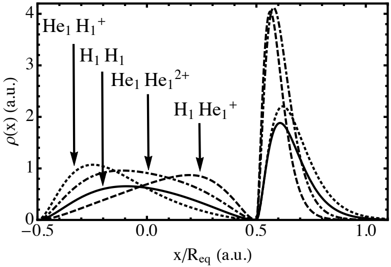


Two-electron diatomic molecules in 1D

Potential energy curves for the H_2 molecule

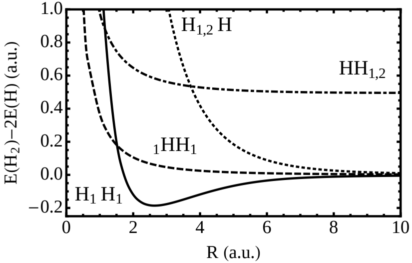


Electron densities for two-electron diatomics

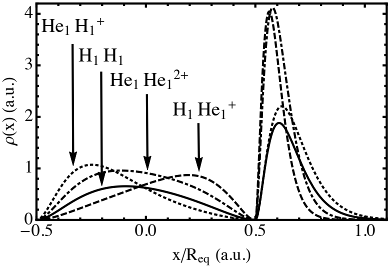


Two-electron diatomic molecules in 1D

Potential energy curves for the H_2 molecule

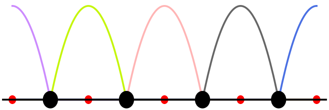


Electron densities for two-electron diatomics



1D atoms are bound by one-electron bonds!!

Lego-style formation of 1D polymers



- A single H_1 atom has a dipole moment

⇒ Two H_1 atoms will feel dipole-dipole attraction

$$\overrightarrow{H_1} + \overrightarrow{H_1} \longrightarrow \overrightarrow{H_1 H_1}$$

- The resulting H_1H_1 molecule also has a dipole moment

⇒ H_1H_1 and H_1 will feel dipole-dipole attraction

$$\overrightarrow{H_1 H_1} + \overrightarrow{H_1} \longrightarrow \overrightarrow{H_1 H_1 H_1}$$

- The resulting $H_1H_1H_1$ molecule also has a dipole moment

⇒ $H_1H_1H_1$ and H_1 will feel dipole-dipole attraction

$$\overrightarrow{H_1 H_1 H_1} + \overrightarrow{H_1} \longrightarrow \overrightarrow{H_1 H_1 H_1 H_1}$$

Take-home messages

- All uniform electron gases are equal, but some are more equal than others!
- GLDA improves LDA (a lot)
- 1D chemistry is very different from 3D chemistry
- Electrons cannot penetrate the nuclei
- Periodic Table has only two groups: alkali metals and noble gases
- Dipole-dipole contribution to bonding is important
- 1D atoms are bound by one-electron bonds!