Generalized Local Density Approximation in One Dimension

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QMC in the Apuan Alps VIII,
Vallico Sotto, Tuscany
1st August 2013

My collaborator (and former boss)

Prof. Peter Gill

- Professor at ANU since 2004
- Nottingham (1999-2004)
- Cambridge (1996-1999)
- Massey University (1993-1996)
- Postdoc with Pople (1989-1993)

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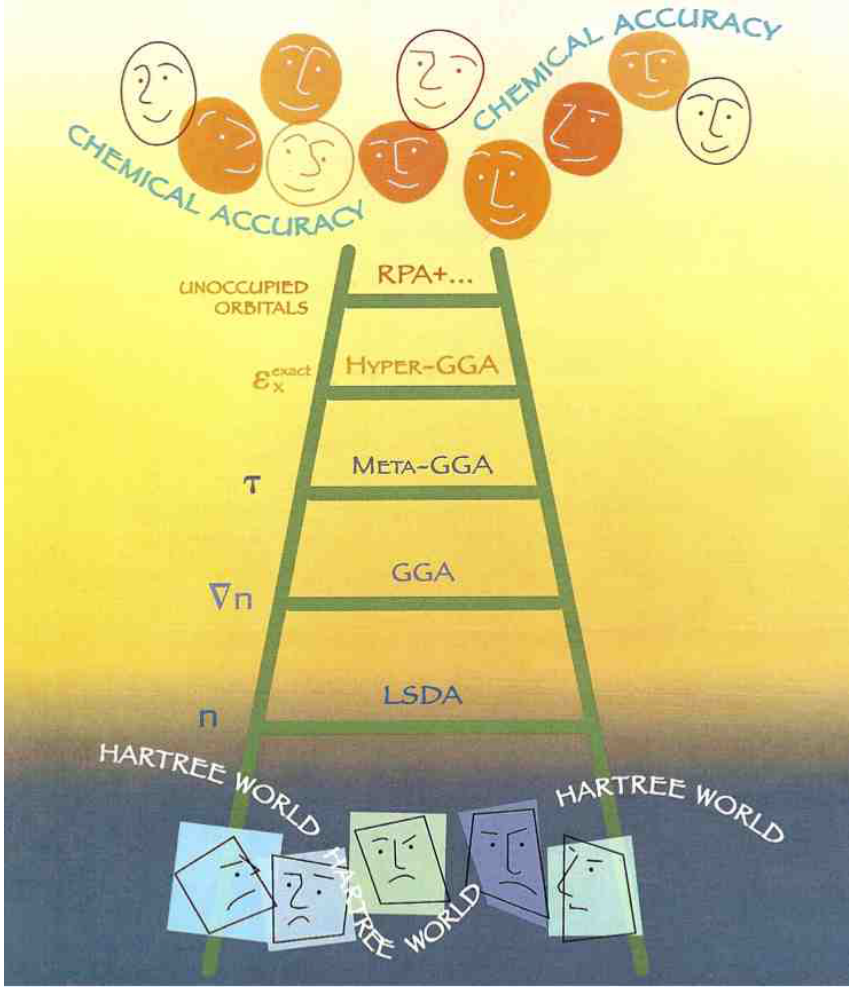
☹☹ Not very accurate for correlation energy (overestimated by roughly 200%)

Jacob's ladder vs Generalized LDA idea

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



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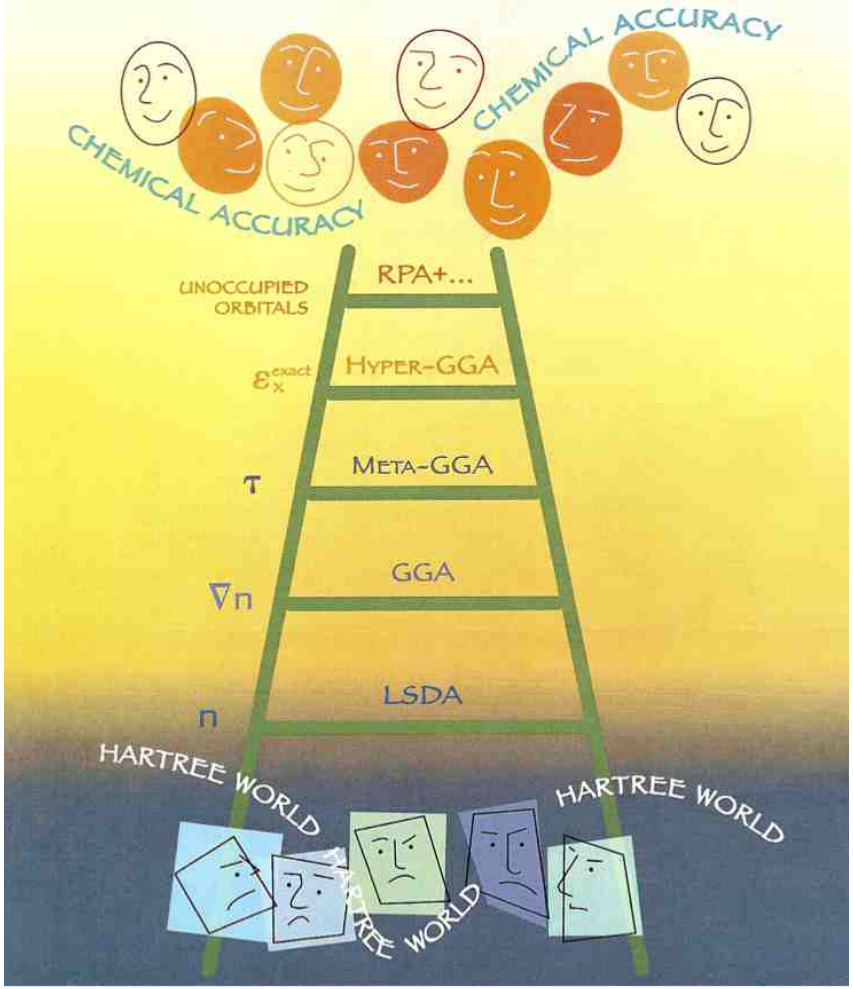

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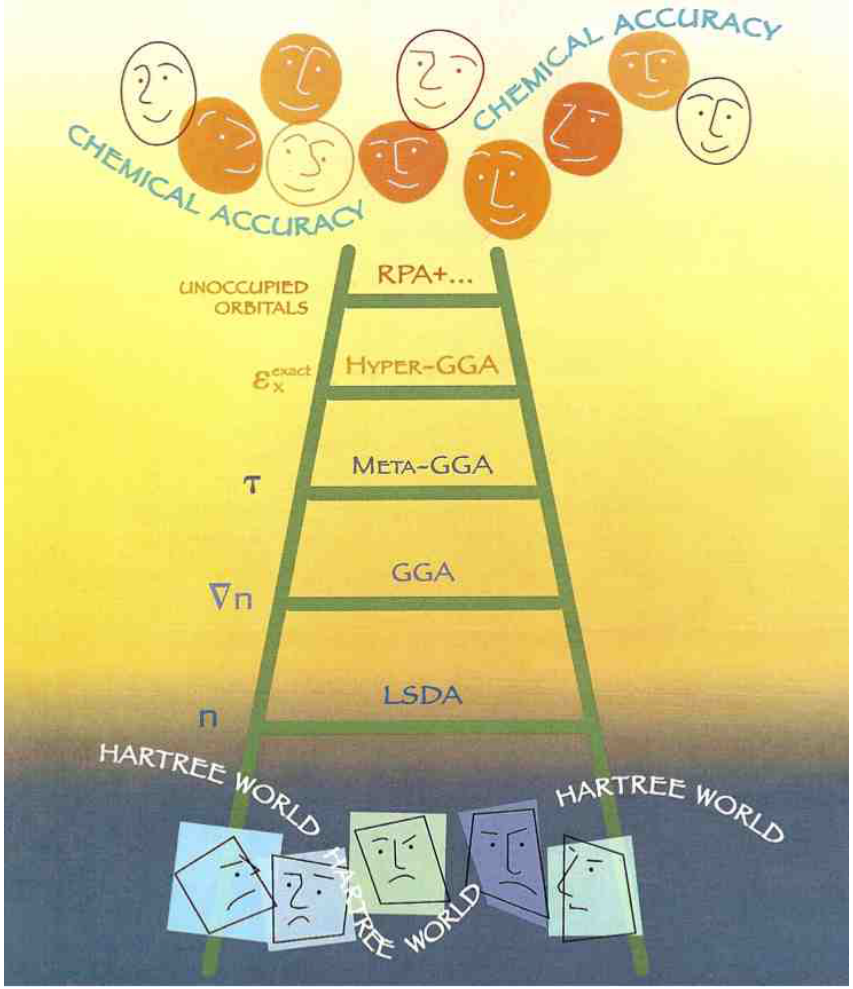

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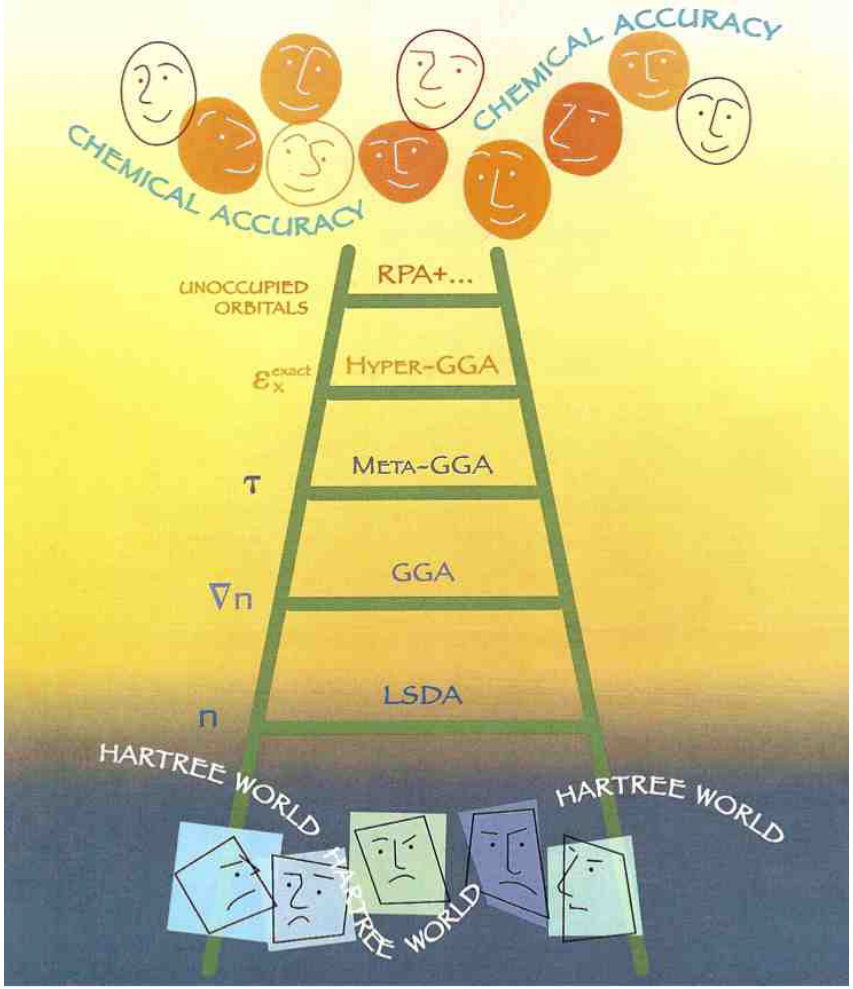
- We add a new local two-electron parameter η



Generalized LDA: Hole curvature

- Suppose that an electron is at the point $\mathbf{r}$.
- The probability that another electron lies at a distance u is

$$P(u|\mathbf{r}) = \frac{\int \rho_2(\mathbf{r}, \mathbf{r}+\mathbf{u}) d\Omega_u}{\rho(\mathbf{r})}$$

  where Ω_u is the angular part of u and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is the reduced 2nd-order density matrix
- $P''(0|\mathbf{r})$ indicates the width of the hole around the electron at $\mathbf{r}$.
- Therefore, the dimensionless curvature

$$\boxed{\eta(\mathbf{r}) = r_s(\mathbf{r})^3 P''(0|\mathbf{r})}$$

  measures of the proximity of other electrons to an electron at $\mathbf{r}$.

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Infinite UEG

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  4. In the limit as $n \to \infty$ and $V \to \infty$, one obtains an infinite UEG

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Finite UEGs

- One can also construct UEGs using a finite number of electrons

Loos & Gill, *J Chem Phys* 135 (2011) 214111
Gill & Loos, *Theor Chem Acc* 131 (2012) 1069

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☺☺☺ For $n \to \infty$, we get the infinite UEG!!

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Uniform electron gases

A Few Finite UEGs

$\mathcal{D}$	System	Name
1	n electrons on a ring	n-ringium
2	n electrons on a sphere	n-spherium
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Ringium: "— *One Ring to Rule Them All* —"

Electrons on a Ring

Wavefunctions & Energies

$$\hat{H} = -\frac{1}{2R^2}\sum_{i=1}^{n}\frac{\partial^2}{\partial\theta_i^2} + \sum_{i<j}^{n}\frac{1}{r_{ij}}$$

$$\varepsilon = ? \qquad \Psi = ?$$

$$r_s = \frac{1}{2\rho} = \frac{\pi R}{n}$$

Remarque: the electrons interact "through" the ring

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  Mitas, *Phys Rev Lett* 96 (2006) 240402

When $r_{12} \to 0$,

$$\boxed{\Psi(r_{12}) = r_{12}\left(1 + \frac{r_{12}}{2}\right) + O(r_{12}^3)}$$

Loos & Gill, *Phys Rev Lett* 108 (2012) 083002

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- The system is spin-blind:
  - The divergence of the Coulomb operator mimics the Pauli principle
  - Ferromagnetic and paramagnetic states are degenerate
  - The fermonic and bosonic states are degenerate (Bose-Fermi mapping)

  Lee & Drummond, *Phys Rev B* 83 (2011) 245114
  Astrakharchik & Girardeau, *Phys Rev B* 83 (2011) 153303

Hartree-Fock approximation for n-ringium

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- The HF wave function and the η parameter are

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- The HF energy is

$$\varepsilon_{\text{HF}} = \frac{n^2 - 1}{n^2} \frac{\pi^2}{24\, r_s^2} + \frac{1}{4\, r_s} \left(\sum_{k=1}^{n} \frac{4 - 1/n^2}{2k - 1} - 3 \right)$$

Loos & Gill, *J Chem Phys* 138 (2013) 164124

1st weapon: Perturbation expansions

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- We can also find the low-density expansion coefficients (valid for $r_s \gg 1$)

$$\boxed{\varepsilon_c = \frac{\gamma_2}{r_s} + \frac{\gamma_3}{r_s^{3/2}} + \ldots}$$

Loos, *J Chem Phys* 138 (2013) 064108
Loos & Gill, *J Chem Phys* 138 (2013) 164124

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- ☺ Hylleraas-type calculations can be done for few electrons
- ☺ It works well for intermediate r_s
- ☹ However, the many-electron integrals are too numerous and too difficult for larger number of electrons
- So how can we calculate accurate energies for intermediate r_s?

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  2. Accurate DMC energies depend on accurate nodes

☺☺☺ Fortunately, the HF nodes (*i.e.* $r_{ij} = 0$) are exact! Youpi!

$$\Psi_{\text{Trial}}(\{r_{ij}\}) = \Psi_{\text{HF}}(\{r_{ij}\}) \prod_{i<j}^{n} \left(\sum_{k} c_k r_{ij}^k \right)$$

Just in case someone is interested: Exact solutions for $n = 2$

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- The Schrödinger eqn is separable in extracule & intracule coordinates
- The extracule equation is trivial to solve
- The intracule equation is a Heun-type differential equation
- For certain "eigenradi" R, both ϵ and Ψ can be obtained in closed form
- There are a countably infinite number of these closed-form solutions

Loos & Gill, *Phys Rev Lett* 103 (2009) 123008; *ibid* 108 (2012) 083002

Some exact solutions

State	R	ε	$\Psi(r_{12})$	$x = r_{12}/(2R)$
Ground	$1/2$	$9/4$	$r_{12}\sqrt{1+x}$	
	$\sqrt{3/2}$	$2/3$	$r_{12}\left[1+\frac{1}{2}r_{12}\right]$	
	$\frac{1}{4}(\sqrt{33}+3)$	$\frac{25}{96}(7-\sqrt{33})$	$r_{12}\sqrt{1+x}\left[1+(R-\frac{1}{2})x\right]$	
	$\sqrt{23/2}$	$9/46$	$r_{12}\left[1+\frac{1}{2}r_{12}+\frac{5}{2}x^2\right]$	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	
1st excited	$\frac{1}{4}(\sqrt{33}-3)$	$\frac{25}{96}(7+\sqrt{33})$	$r_{12}\sqrt{1-x}\left[1+(R+\frac{1}{2})x\right]$	
	$\sqrt{5/2}$	$9/10$	$r_{12}\sqrt{1-x}\sqrt{1+x}\left[1+\frac{1}{2}r_{12}\right]$	
	$\sqrt{33/2}$	$8/33$	$r_{12}\sqrt{1-x}\sqrt{1+x}\left[1+\frac{1}{2}r_{12}+\frac{7}{2}x^2\right]$	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	

Loos & Gill *Phys Rev Lett* 108 (2012) 083002

Reduced correlation energies ($\mathrm{m}E_\mathrm{h}$) for n-ringium

Combining perturbation expansions, Hylleraas and DMC calculations leads to

		Seitz radius r_s								
n	$6\eta/\pi^2$	0	0.1	0.2	0.5	1	2	5	10	20
2	3/4	13.212	12.985	12.766	12.152	11.250	9.802	7.111	4.938	3.122
3	8/9	18.484	18.107	17.747	16.755	15.346	13.179	9.369	6.427	4.030
4	15/16	21.174	20.698	20.249	19.027	17.324	14.762	10.390(0)	7.085(0)	4.425(0)
5	24/25	22.756	22.213	21.66(2)	20.33(1)	18.439(1)	15.644(2)	10.946(0)	7.439(0)	4.636(0)
6	35/36	23.775	23.184	22.63(2)	21.14(1)	19.137(1)	16.192(2)	11.285(0)	7.653(0)	4.762(0)
7	48/49	24.476	23.850	23.24(2)	21.70(1)	19.607(1)	16.554(2)	11.509(0)	7.795(0)	4.844(0)
8	63/64	24.981	24.328	23.69(3)	22.11(1)	19.940(1)	16.808(2)	11.664(0)	7.890(0)	4.901(0)
9	80/81	25.360	24.686	24.04(2)	22.39(1)	20.186(1)	16.995(3)	11.777(0)	7.960(0)	4.941(0)
10	99/100	25.651	24.960	24.25(4)	22.62(1)	20.373(1)	17.134(2)	11.857(0)	8.013(0)	4.973(0)
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
∞	1	27.416	26.597	25.91(1)	23.962(1)	21.444(0)	17.922(0)	12.318(0)	8.292(0)	5.133(0)

Lee & Drummond, *Phys Rev B* 83 (2011) 245114

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1. "Robust" interpolation
   Cioslowski, *J Chem Phys* 136 (2012) 044109
2. Fitting based on hypergeometric functions
   (maybe related to the ISI functional of Seidl and Perdew)
   Seidl, Perdew & Kurth, *Phys Rev Lett* 84 (2000) 5070

Take-home messages

How can we use these new UEG results?

- n electrons on a ring gives UEGs of any desired density ρ
- We have calculated their correlation energies very accurately
- Our results permit a generalization of the LDA for finite systems
- This improves the accuracy of the lowest rung of Jacob's Ladder
- Next, we will extend this approach to electrons in 2D and 3D