Generalized Local Density Approximation in One Dimension

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My collaborator (and former boss)

Prof. Peter Gill

- Professor at the RSC (ANU) since 2004
- Pople Medal (2005)
- Schrödinger Medal (2011)
- Fukui Medal (2013)

The Local Density Approximation (LDA) in DFT

- Find the properties of the uniform electron gas (UEG)
- Treat a molecular density as a collection of tiny bits of UEG

☺ The LDA is an *ab initio* model with no adjustable parameters

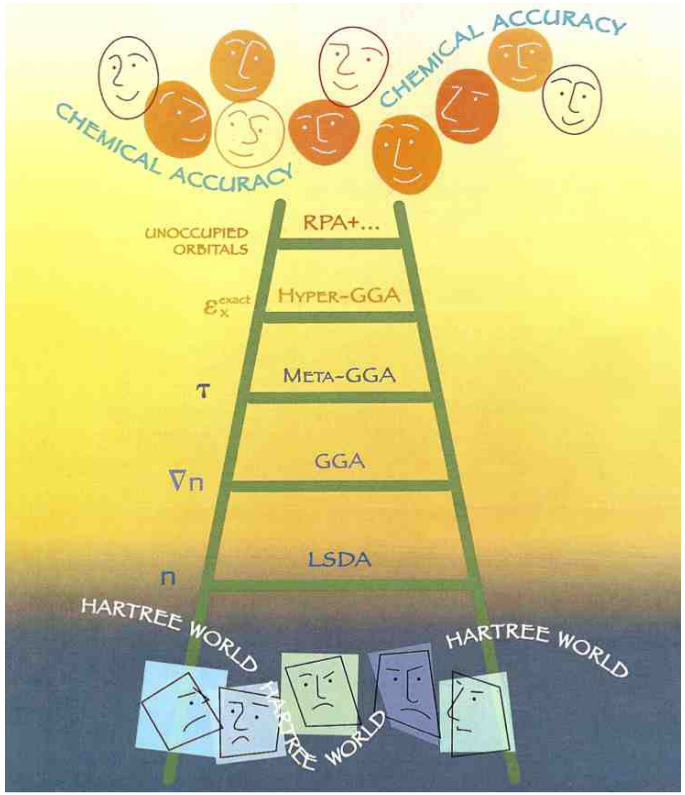
☺ This is an attractive approach to molecular electronic structure

☺ It also forms a foundation for more accurate approximations

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

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!
- We propose to follow an alternative route to heaven!
- We add a new two-electron parameter η



Generalized LDA

Hole curvature (Part 1)

- 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 second-order density matrix.

Generalized LDA

Hole curvature (Part 2)

- $P(u|\mathbf{r})$ depends on $\mathbf{r}$ but, at a given $\mathbf{r}$, it is easy to show that

$$\int_0^\infty P(u|\mathbf{r})du = n - 1$$

- $P''(0|\mathbf{r})$ indicates the width of the hole around the electron at $\mathbf{r}$.

- Therefore, the dimensionless curvature

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

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

Uniform electron gases

Infinite UEGs

- One of the most popular models in condensed matter physics
- The recipe:
  1. Put n electrons into a $\mathcal{D}$-dimensional cube of volume V
  2. Add a background positive charge to achieve neutrality
  3. Increase both n and V so that $\rho = n/V$ remains constant
  4. In the limit as $n \to \infty$ and $V \to \infty$, one obtains an infinite UEG

Ceperley & Alder, *Phys Rev Lett* 45 (1980) 566

Uniform electron gases

Finite UEGs

- One can also construct UEGs using a finite number of electrons
- The recipe:
  1. Put n electrons onto a $\mathcal{D}$-dimensional sphere
  2. Add a background positive charge to achieve neutrality if you wish
- That's all

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

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
3	n electrons on a glome	n-glomium
⋮	⋮	⋮

Ringium: "— *One Ring to Rule Them All* —"

Electrons on a Ring

Wavefunctions & Energies

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

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

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

Hartree-Fock approximation for n-ringium

- The HF wave function and the η parameter are

$$\Phi_{\text{HF}} = \prod_{i<j}^{n} \hat{r}_{ij} \qquad \eta = \left(1 - \frac{1}{n^2}\right) \frac{\pi^2}{6}$$

where $\hat{r}_{ij}$ is the signed interelectronic distance.

- 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

- We can find the small-r_s expansion coefficients (valid for $r_s \ll 1$)

$$\boxed{\varepsilon = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \varepsilon_0 + \varepsilon_1 \, r_s + \ldots}$$

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

$$\boxed{\varepsilon = \frac{\eta_2}{r_s} + \frac{\eta_3}{r_s^{3/2}} + \frac{\eta_4}{r_s^2} + \ldots}$$

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

2nd weapon: Hylleraas calculations

- ☺ 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?

3rd weapon: Quantum Monte Carlo

- Diffusion Monte Carlo calculations offer a way forward

☹ These converge poorly in the small-r_s regime

☺ These converge well in the medium-r_s regime

☺☺ These converge very well in the large-r_s regime

- Weaknesses?
  1. DMC energies have some (controllable) statistical noise
  2. Accurate DMC energies depend on accurate nodes

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

In passing: Exact solutions for $n = 2$

- 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* 108 (2012) 083002

Some exact solutions

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

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

		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	13.179	10.390	7.085	4.425
5	24/25	22.756	22.213	21.66	20.33	18.439	15.644	10.946	7.439	4.636
6	35/36	23.775	23.184	22.63	21.14	19.137	16.192	11.285	7.653	4.762
7	48/49	24.476	23.850	23.24	21.70	19.607	16.554	11.509	7.795	4.844
8	63/64	24.981	24.328	23.69	22.11	19.940	16.808	11.664	7.890	4.901
9	80/81	25.360	24.686	24.04	22.39	20.186	16.995	11.777	7.960	4.941
10	99/100	25.651	24.960	24.25	22.62	20.373	17.134	11.857	8.013	4.973
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
∞	1	27.416	26.597	25.91	23.962	21.444	17.922	12.318	8.292	5.133

Lee & Drummond *Phys Rev B* 83 (2010) 245114

Fitting the results (under progress)

- We know the high-density and low-density expansions
- We should fit our results with functions that behave this way
- But which functions should we choose?

1. "Robust" interpolation
   Cioslowski, *J Chem Phys* 136 (2012) 044109
2. Fitting based on hypergeometric functions
   (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 Jacobs Ladder
- Next, we will extend this approach to electrons in 2D and 3D