# Lessons from electron(s) on sphere(s)

Pierre-François Loos and Peter Gill

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Mathematical Methods in Quantum Chemistry Oberwolfach, Germany June 27th 2011

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Introduction		
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Motivations		

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Introduction		
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Motivations		

Arguments for high-impact journals

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Introduction	Two electrons on a (hyper)sphere	Uniform electron gases	
Motivations			

### Arguments for high-impact journals

Multielectron bubbles in liquid helium





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### Arguments for high-impact journals

- Multielectron bubbles in liquid helium
- Arrangements of protein subunits on spherical viruses





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### Arguments for high-impact journals

- Multielectron bubbles in liquid helium
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- Fullerene-like molecules: C<sub>60</sub>, C<sub>240</sub>, C<sub>540</sub>, ...



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### Our arguments...



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This is mathematically challenging



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- This is mathematically challenging
- This is actually related to "real" systems



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### Our arguments...

- This is mathematically challenging
- This is actually related to "real" systems
- It yielded a number of unexpected discoveries



	Two electrons on a (hyper)sphere	Uniform electron gases	
	0000		
Spherium			

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	Two electrons on a (hyper)sphere	Uniform electron gases	
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Spherium			

#### One electron on a sphere



$$\hat{H} = -rac{1}{2}
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Solution:

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**Solution**:  $Y_{\ell m}(\theta, \phi) \Rightarrow \text{Boring}!!!$ 

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Solution:

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 $\hat{H} = -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{1}{r_{12}}$ 

Two electrons on a sphere

	Two electrons on a (hyper)sphere		
	• <b>0</b> 00		
Spherium			

#### One electron on a sphere



$$\hat{H} = -\frac{1}{2}\nabla^2$$

### **Solution**: $Y_{\ell m}(\theta, \phi) \Rightarrow \text{Boring}!!!$

Solution:  $??? \Rightarrow \text{Exciting}!!!$ 

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Lessons from electron(s) on sphere(s)

### Two electrons on a sphere



$$\hat{H}=-rac{1}{2}\left(
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$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1\right)\frac{d^2}{dr_{12}^2} + \left(\frac{3r_{12}}{4R^2} - \frac{1}{r_{12}}\right)\frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

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Note: related to the Heun's differential equation



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#### **Frobenius method**

We seek polynomial solutions: 
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\ell=0}^{\infty} c_\ell r_{12}^\ell$$

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#### **Frobenius method**

We seek polynomial solutions:  $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\ell=0}^{\infty} c_{\ell} r_{12}^{\ell}$ 

#### **Analytical solutions**

$$R = \sqrt{3}/2 \quad E = 1 \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2) = 1 + r_{12}$$
  

$$R = \sqrt{7} \qquad E = 2/7 \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2) = 1 + r_{12} + \frac{5}{28}r_{12}^2$$
  

$$\vdots \qquad \vdots \qquad \vdots$$

#### Loos & Gill Phys Rev Lett 103 (2009) 123008

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	Two electrons on a (hyper)sphere		
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Glomium			

#### What is a "glome"?

A glome is a 3-sphere, i.e. the surface of a 4-dimensional ball



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Hamiltonian of the ground state

$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1\right)\frac{d^2}{dr_{12}^2} + \left(\frac{5r_{12}}{4R^2} - \frac{2}{r_{12}}\right)\frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

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#### **Analytical solutions**

:

$$R = \sqrt{10}/2 \quad E = 1/2 \quad \Psi(\mathbf{r}_1, \mathbf{r}_2) = 1 + \frac{1}{2}r_{12}$$
  

$$R = \sqrt{66}/2 \quad E = 2/11 \quad \Psi(\mathbf{r}_1, \mathbf{r}_2) = 1 + \frac{1}{2}r_{12} + \frac{7}{132}r_{12}^2$$

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	Two electrons on a (hyper)sphere	Uniform electron gases	
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Exact solutions in D din	nensions		

### Generalization to a D-dimensional space

#### First exact solutions for a *D*-sphere

State	D	2 <i>R</i>	Ε	$\Psi(\mathbf{r}_1,\mathbf{r}_2)$
	1	$\sqrt{6}$	2/3	$r_{12}(1 + r_{12}/2)$
1 <b>S</b>	2	$\sqrt{3}$	1	$1 + r_{12}$
5	3	$\sqrt{10}$	1/2	$1 + r_{12}/2$
	4	$\sqrt{21}$	1/3	$1 + r_{12}/3$
	1	$\sqrt{6}$	1/2	$1 + r_{12}/2$
3 D	2	$\sqrt{15}$	1/3	$1 + r_{12}/3$
,	3	$\sqrt{28}$	1/4	$1 + r_{12}/4$
	4	$\sqrt{45}$	1/5	$1 + r_{12}/5$

Loos & Gill Phys Rev Lett 103 (2009) 123008; Mol Phys 108 (2010) 2527

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Jellium paradigm			

The 2D- and 3D-jellium model

Giuliani & Vignale, Quantum theory of electron liquid

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#### The 2D- and 3D-jellium model

Jellium is the main ingredient of many (but not all) DFT functionals

#### Giuliani & Vignale, Quantum theory of electron liquid

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### The 2D- and 3D-jellium model

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- n electrons in a square/cubic box of volume V embedded in a positive "jelly" background
- Uniform electron density at all points only if  $n \to \infty$  and  $V \to \infty$
- Characterized by one parameter: the Seitz radius r<sub>s</sub>

Giuliani & Vignale, Quantum theory of electron liquid

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L-spherium and L-glomiu	ım		

# Uniform electron gas in Sphereland

We fill each (hyper)spherical harmonic  $Y_{\ell m(n)}$  up to  $\ell = L$  with one upand one down-electron

### Loos & Gill Phys Rev B (submitted) arXiv:1101.3131

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and one down-electron  $r_{\ell m(n)}$  up to  $\ell = L$  with one up

#### L-Spherium

$$\sum_{m=-\ell}^{+\ell} |Y_{\ell m}(\theta,\phi)|^2 = \frac{2\ell+1}{4\pi}$$

$$n = 2(L+1)^2$$
$$\rho = \frac{(L+1)^2}{2\pi R^2} = \frac{1}{\pi r_s^2}$$

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#### L-Spherium

#### L-Glomium

$$\sum_{m=-\ell}^{+\ell} |Y_{\ell m}(\theta,\phi)|^2 = \frac{2\ell+1}{4\pi}$$

$$\sum_{m=0}^{\ell} \sum_{n=-m}^{+m} |Y_{\ell m n}(\chi,\theta,\phi)|^2 = \frac{(\ell+1)^2}{2\pi^2}$$

$$n = 2(\ell+1)^2 \qquad n = 2(\ell+1)(\ell+3/2)(\ell+2)/3$$

$$\rho = \frac{(\ell+1)^2}{2\pi R^2} = \frac{1}{\pi r_s^2} \qquad \rho = \frac{(\ell+1)(\ell+3/2)(\ell+2)/3}{6\pi^2 R^3} = \frac{3}{4\pi r_s^3}$$

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			Flatland vs. Sphereland	
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L-spherium vs. 2D-jelliu	m			

$$\bar{E}_{\text{2D-jell}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + (\varepsilon_{0,J} + \varepsilon_{0,K}) + \lambda_1 r_s \ln r_s + O(r_s)$$

$$\varepsilon_{-2} =$$

 $\varepsilon_{-1} =$ 

 $\varepsilon_{0,J} =$ 

 $\varepsilon_{0,K} =$ 

$$\lambda_1 =$$

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$$\varepsilon_{-2} = + \frac{L(L+2)}{2(L+1)^2}$$

$$\varepsilon_{-1} = -\frac{1}{\sqrt{2}} F \begin{bmatrix} -L, L+2, \frac{1}{2}, -\frac{1}{2} \\ -L-\frac{1}{2}, L+\frac{3}{2}, 2 \end{bmatrix}$$

$$\varepsilon_{0,J} = -\frac{2}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle^2}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\varepsilon_{0,K} = \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j}$$

$$\lambda_1 = (\text{resummation})$$

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$$\begin{split} \varepsilon_{-2} &= + \frac{L(L+2)}{2(L+1)^2} & \longrightarrow + \frac{1}{2} \\ \varepsilon_{-1} &= -\frac{1}{\sqrt{2}} F \begin{bmatrix} -L, L+2, \frac{1}{2}, -\frac{1}{2} \\ -L-\frac{1}{2}, L+\frac{3}{2}, 2 \end{bmatrix} & \longrightarrow - \frac{4\sqrt{2}}{3\pi} \\ \varepsilon_{0,J} &= -\frac{2}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle^2}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} & \longrightarrow \ln 2 - 1 \\ \varepsilon_{0,K} &= \frac{1}{n} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij|ab\rangle\langle ba|ij\rangle}{\kappa_a + \kappa_b - \kappa_i - \kappa_j} & \longrightarrow G - \frac{8}{\pi^2}\beta(4) \\ \lambda_1 &= \text{(resummation)} & \longrightarrow - \sqrt{2}\left(\frac{10}{3\pi} - 1\right) \end{split}$$

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L-glomium vs. 3D-jellium					

$$\bar{E}_{\text{3D-jell.}}(r_s) = \frac{\varepsilon_{-2}}{r_s^2} + \frac{\varepsilon_{-1}}{r_s} + \lambda_0 \ln r_s + (\varepsilon_{0,\text{J}} + \varepsilon_{0,\text{K}}) + O(r_s \ln r_s)$$

 $\varepsilon_{-2}$ 

 $\varepsilon_{-1}$ 

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 $\lambda_0$ 

 $\varepsilon_{0,K}$ 

P.-F. Loos — http://rsc.anu.edu.au/~loos/ — Lessons from electron(s) on sphere(s)

			Flatland vs. Sphereland		
			00		
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$$\begin{array}{cccc} \varepsilon_{-2} & \xrightarrow{L \to \infty} & +\frac{3}{10} \left(\frac{9\pi}{4}\right)^{2/3} & \checkmark \\ \varepsilon_{-1} & \xrightarrow{L \to \infty} & -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} & \checkmark \\ \lambda_{0} & \xrightarrow{\text{resum.}} & \frac{1-\ln 2}{\pi^{2}} & \checkmark \\ \varepsilon_{0,J} & \xrightarrow{\text{resum.}} & -0.071099 & \checkmark \\ \varepsilon_{0,K} & \xrightarrow{L \to \infty} & \frac{\ln 2}{6} - \frac{3}{4\pi^{2}} \zeta(3) & \checkmark \end{array}$$

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**Conjecture:** high-density expansions identical to all order!!

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		Conclusion
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Final remarks		

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		Conclusion
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**Two-electron systems** 



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#### **Two-electron systems**

O-spherium and O-glomium are exactly solvable two-electron systems

Final remarks				Conclusion
	Final remarks	00	00	

#### **Two-electron systems**

- O-spherium and O-glomium are exactly solvable two-electron systems
- Cusp conditions are identical to real systems

	Two electrons on a (hyper)sphere		Conclusion
Final remarks			

#### **Two-electron systems**

- 0-spherium and 0-glomium are exactly solvable two-electron systems
- Cusp conditions are identical to real systems

#### Uniform electron gases

	Two electrons on a (hyper)sphere		Conclusion
Final remarks			

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#### Uniform electron gases

Spherium and glomium are uniform electron gases for any value of L

		Conclusion
		•
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- They appear to have identical properties to jellium when  $L \rightarrow \infty$ ⇒ "short-sightedness" of electronic matter

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	Two electrons on a (hyper)sphere	Uniform electron gases OO	Flatland vs. Sphereland OO	Conclusion
Final remarks				

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Final remarks				Conclusion
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- It seems to be true in the low-density  $(r_s \to \infty)$  limit as well (Thomson problem)
- They might be more convenient models for DFT functional development