Lessons from electron(s) on a (hyper)sphere

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My collaborator

Prof. Peter Gill

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

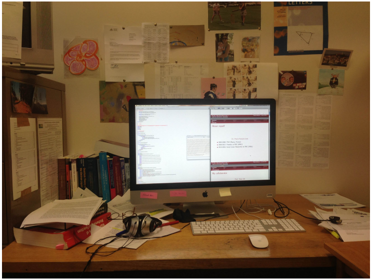
About myself

Dr. Pierre-François (Titou) Loos

- **2005-2008**:
  PhD (Nancy, France)
  funded by the French government

- **2009-2012**:
  Postdoc at the RSC (ANU)
  funded by the ARC (DP)

- **2013-2016**:
  Early Career Researcher at the RSC
  funded by the ARC (DECRA)



Why bother with electron correlation?

Definition: $E_{\text{corr}} = E_{\text{exact}} - E_{\text{Hartree-Fock}}$

- ☺ HF theory ignores correlation and gives 99% of the energy
- ☺ It is often accurate for the prediction of molecular structures
- ☺ It is computationally cheap and can be applied to large systems
- ☹ Unfortunately, the final 1% can have important chemical effects
- ☹ This is particularly true when bonds are broken and/or formed
- ☹ Thus, realistic chemistry requires a good treatment of correlation

Some random thoughts on electron correlation

- The concept was introduced at the dawn of quantum chemistry
  Wigner Phys Rev 46 (1934) 1002
- Its definition was agreed somewhat later
  Löwdin Adv Chem Phys 2 (1959) 207

- ☹ One Nobel Laureate used to refer to it as "the stupidity energy"
  Feynmann (1972)
- ☺ There have been recent heroic calculations on the helium atom
  Nakashima & Nakatsuji J Chem Phys 127 (2007) 224104
- ☹ "We conclude that theoretical understanding here lags well behind the power of available computing machinery"
  Schwartz Int J Mod Phys E 15 (2006) 877

The helium-like ions: One nucleus of charge Z and Two electrons

The Hamiltonian operator

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}, \quad \text{where } r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| .$$

- $Z = 1$ gives the H^- anion
- $Z = 2$ gives the He atom
- $Z = 3$ gives the Li^+ cation
- $Z = 4$ gives the Be^{2+} cation
- etc.

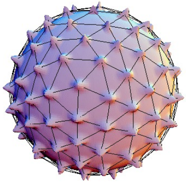
History of accurate calculation on the He atom

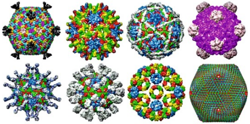
"For thousands of years mathematicians have enjoyed competing with one other to compute ever more digits of the number π. Among modern physicists, a close analogy is computation of the ground state energy of the helium atom, begun 75 years ago by E. A. Hylleraas."
Schwartz Int J Mod Phys E 15 (2006) 877

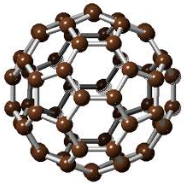
Year	Authors	Energy (a.u.)
1929	Hylleraas	-2.902 43
1957	Kinoshita	-2.903 722 5
1966	Frankowski & Pekeris	-2.903 724 377 032 6
1994	Thakkar & Koga	-2.903 724 377 034 114 4
1998	Goldman	-2.903 724 377 034 119 594
1999	Drake	-2.903 724 377 034 119 596
2002	Sims & Hagstrom	-2.903 724 377 034 119 598 299
2002	Drake et al.	-2.903 724 377 034 119 598 305
2002	Korobov	-2.903 724 377 034 119 598 311 158 7
2006	Schwartz	-2.903 724 377 034 119 598 311 159 245 194 404 440 049 5
2007	Nakashima & Nakatsuji	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37

Nakashima & Nakatsuji J Chem Phys 127 (2007) 224104

Why bother with electron(s) on a sphere?







Arguments for high-impact journals

It can be experimentally realized:

- Multielectron bubbles in liquid helium
- Arrangements of protein subunits on spherical viruses
- Colloid particles in colloidosomes
- Fullerene-like molecules: C_{60}, C_{240}, C_{540}, ...

Our arguments...

- It yielded a number of unexpected discoveries
- This is actually related to “real” Quantum Chemistry

The spherium atom: electron(s) on a sphere of radius R

One electron on a sphere

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

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

Two electrons on a sphere

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

Solution:
??? $\Rightarrow$ Exciting!!!

Loos & Gill Phys Rev A 79 (2009) 062517

Let's play the game: numerical calculations

First, we solved the Schrödinger equation numerically, e.g.

$$R = 1, \qquad E_{\mathrm{Sp}} = 0.852\,781\,065\,056\,462\,665\,400\,437\,966\,038\,710\,264\ldots$$
$$R = 100, \qquad E_{\mathrm{Sp}} = 0.005\,487\,412\,426\,784\,081\,726\,642\,485\,484\,213\,968\ldots$$

Observation:

— With a small expansion $\psi = \sum_k c_k r_{12}^k$, one can get many digits! —

Is it trying to tell us something?

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Hamiltonian of the ground state

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

Frobenius method

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

Analytical solutions

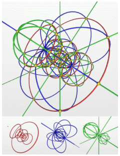
$$\begin{array}{lll}
R = \sqrt{3}/2 & E = 1 & \Psi(\mathbf{r}_1,\mathbf{r}_2) = 1 + r_{12} \\
R = \sqrt{7} & E = 2/7 & \Psi(\mathbf{r}_1,\mathbf{r}_2) = 1 + r_{12} + \frac{5}{28} r_{12}^2 \\
\vdots & \vdots & \vdots
\end{array}$$

Loos & Gill Phys Rev Lett 103 (2009) 123008

The glomium atom: electron(s) on a glome

What is a "glome"?

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



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

Analytical solutions

$$\begin{array}{lll} R = \sqrt{10}/2 & E = 1/2 & \Psi(\mathbf{r}_1,\mathbf{r}_2) = 1 + \frac{1}{2} r_{12} \\ R = \sqrt{66}/2 & E = 2/11 & \Psi(\mathbf{r}_1,\mathbf{r}_2) = 1 + \frac{1}{2} r_{12} + \frac{7}{132} r_{12}^2 \\ \vdots & \vdots & \vdots \end{array}$$

Generalization to a D-dimensional space

Simplest exact solutions for a D-sphere

State	D	$4R^2$	E	$\Psi(\mathbf{r}_1,\mathbf{r}_2)$
	1	6	$2/3$	$r_{12}(1+r_{12}/2)$
	2	3	1	$1+r_{12}$
	3	10	$1/2$	$1+r_{12}/2$
^1S	4	21	$1/3$	$1+r_{12}/3$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$
	D	$(2D-1)(D-1)$	$1/(D-1)$	$1+r_{12}/(D-1)$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$

— Kato's cusp conditions are identical to real systems —

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

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

Two Electrons on a Ring

Wavefunctions & Energies

$$\hat{H} = -\frac{1}{2R^2}\left[\frac{\partial^2}{\partial\theta_1^2} + \frac{\partial^2}{\partial\theta_2^2}\right] + \frac{1}{r_{12}}$$

$$E = ?$$

$$\Psi = ?$$

Separating the Hamiltonian

Let's define the extracule $\Theta = (\theta_1 + \theta_2)/2$ and intracule $\theta = \theta_1 - \theta_2$

Using these coordinates, the Hamiltonian is a sum of two independent parts

$$\hat{H} = -\frac{1}{4R^2}\frac{\partial^2}{\partial\Theta^2} - \frac{1}{R^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{2R\sin(\theta/2)}$$

so we can solve for the extracule and intracule wavefunctions separately.

$$-\frac{1}{4R^2}\frac{d^2}{d\Theta^2}\phi_J = \mathcal{E}_J\phi_J \qquad \left[-\frac{1}{R^2}\frac{d^2}{d\theta^2} + \frac{1}{2R\sin(\theta/2)}\right]\psi_j = \varepsilon_j\psi_j$$

The total wavefunctions and energies are then given by

$$\Psi_{Jj} = \phi_J(\Theta)\psi_j(\theta) \qquad E_{Jj} = \mathcal{E}_J + \varepsilon_j$$

Extracule Schrödinger equation

The Schrödinger equation for the extracule $\Theta = (\theta_1 + \theta_2)/2$ is

$$\boxed{-\frac{1}{4R^2}\frac{d^2}{d\Theta^2}\phi_J = \mathcal{E}_J \phi_J}$$

The resulting wavefunctions and energies are

$$\phi_J = \exp(\imath J \Theta) \qquad \mathcal{E}_J = \frac{J^2}{4R^2}$$

J	0	1	2	3	4	$\cdots$
Symmetry	Σ	Π	Δ	Φ	Γ	$\cdots$

The Σ states ($J = 0$) are uniform electron gases

Intracule Schrödinger equation

The Schrödinger equation for the intracule $\theta = \theta_1 - \theta_2$ is

$$\boxed{\left[-\frac{1}{R^2}\frac{d^2}{d\theta^2} + \frac{1}{2R\sin(\theta/2)}\right]\psi = \varepsilon\,\psi}$$

If we use the distance $u = |\mathbf{r}_1 - \mathbf{r}_2|$, instead of θ, we obtain the Heun-type differential equation

$$\left[\left(\frac{u^2}{4R^2} - 1\right)\frac{d^2}{du^2} + \frac{u}{4R^2}\frac{d}{du} + \frac{1}{u}\right]\psi = \varepsilon\,\psi$$

If we define $x = u/(2R)$, the general solution is

$$\psi = x\,(1+x)^{a/2}\,(1-x)^{b/2}\,P(x)$$

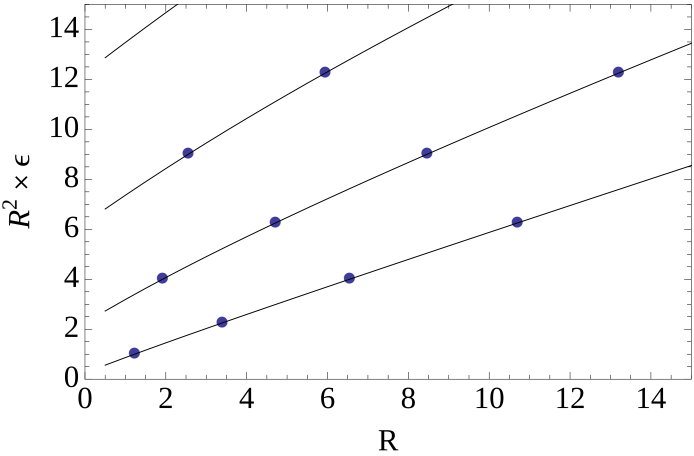
where $a = 0$ or 1, and $b = 0$ or 1, and $P(x)$ is a regular power series in x.

The four families of solutions

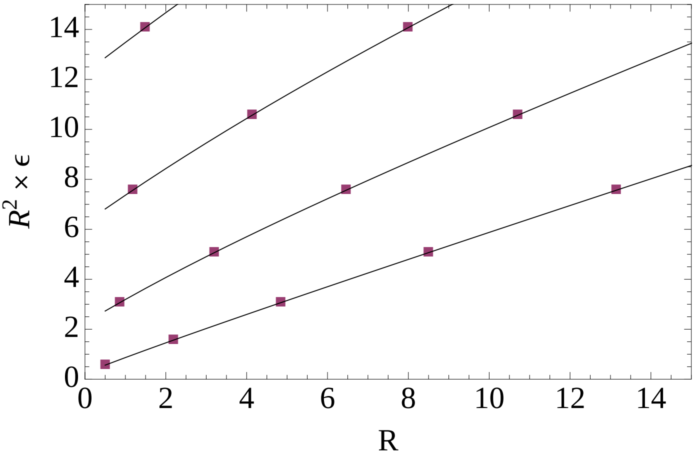
$$\boxed{\psi = x\,(1+x)^{a/2}\,(1-x)^{b/2}\,P(x)}$$

- Four families of solutions: $(a,b) = (0,0)$, $(1,0)$, $(0,1)$ or $(1,1)$
- $b = 0$ yields the ground, 2nd-excited, 4th-excited, etc. states.
- $b = 1$ yields the 1st-excited, 3rd-excited, 5th-excited, etc. states.
- When R is an "eigenradius", $P(x)$ terminates, becoming a polynomial
- In these cases, both ψ and ε can be obtained in closed form
- There are a countably infinite number of these closed-form solutions

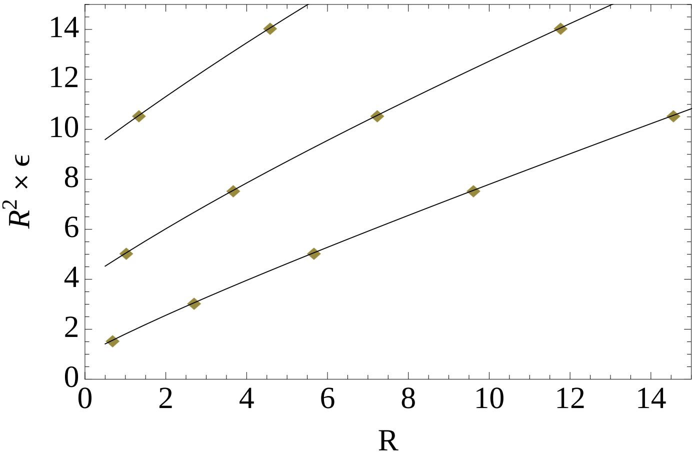
The $(a, b) = (0, 0)$ family



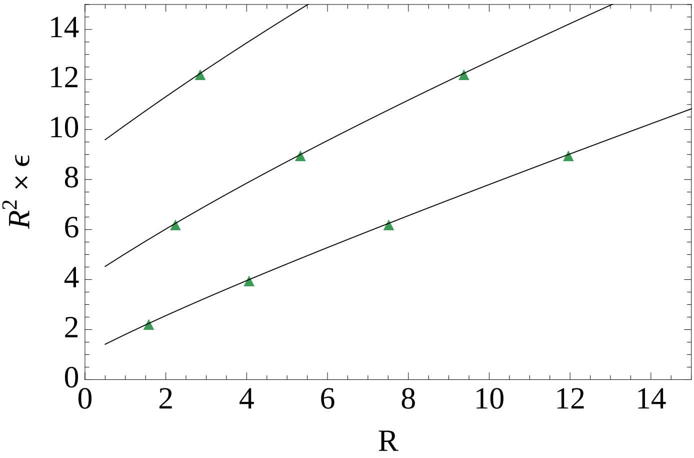
The $(a, b) = (1, 0)$ family



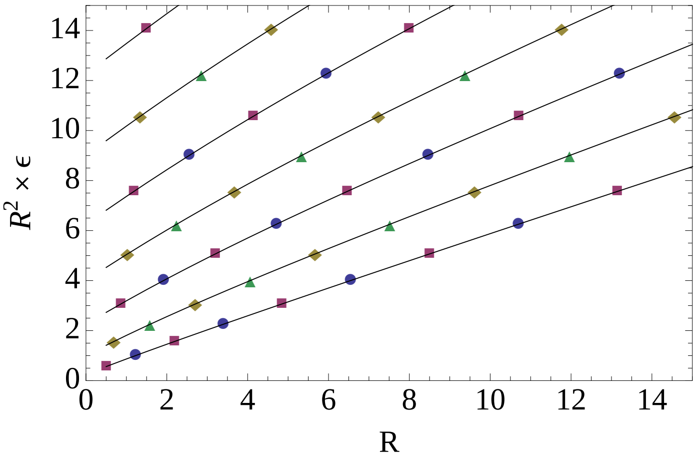
The $(a, b) = (0, 1)$ family



The $(a, b) = (1, 1)$ family



All four families



Some exact closed-form wavefunctions

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

Loos & Gill Phys Rev Lett 108 (2012) 083002

Take-home messages

- Ringium, Spherium and Glomium are exactly solvable two-electron systems
- They shed new light on electron correlation in real systems
- The present method can be generalized to other systems
  Loos Phys Lett A 376 (2012) 1997
  Loos & Gill arXiv:1301.0649
- These systems are uniform electron gases and can be used to develop new exchange-correlation functionals within density-functional theory
  Gill & Loos Theor Chem Acc 131 (2012) 1069
  Loos & Gill J Chem Phys 138 (2013) 164124