Finite Uniform Electron Gases

Peter M.W. Gill

Research School of Chemistry, Australian National University

CECAM workshop: New challenges in RDMFT

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My Collaborators

Marat Sibaev

Postdoc

Davids Agboola

Postdoc

Pierre-François Loos

DECRA Fellow

Outline

INTRODUCTION

In marketing, it is said that a customer has to see an advertisement seven times to remember it.

Marketers like to talk about "The Rule of Seven": the idea that people need to see your marketing message seven times before they take action. . .

(R)D(M)FT

The mathematical problem

- Schrödinger's Equation (time-independent, fixed nuclei, non-relativistic)

$$\hat{\mathbf{H}}\Psi = E\Psi$$

It is an elliptic PDE with $3n$ independent variables ($n \approx 1000$ electrons)

Kato (1957), Hill (1985), Fournais *et al.* (2005), ...

(R)D(M)FT

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- This lecture will focus on the lowest eigenvalue (energy) E

(R)D(M)FT

The mathematical problem

- Schrödinger's Equation (time-independent, fixed nuclei, non-relativistic)

$$\hat{\mathbf{H}}\Psi = E\Psi$$

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Kato (1957), Hill (1985), Fournais *et al.* (2005), ...

- This lecture will focus on the lowest eigenvalue (energy) E
- We usually split the energy into "mean-field" and "non-mean-field" parts

$$E = E_{\mathrm{MF}} + E_c$$

(Easy) $E_{\mathrm{MF}} = \langle \Psi_{\mathrm{MF}} | \hat{\mathbf{H}} | \Psi_{\mathrm{MF}} \rangle \,/\, \langle \Psi_{\mathrm{MF}} | \Psi_{\mathrm{MF}} \rangle$ where Ψ_{MF} is separable

(Hard) E_c can be approximated in a variety of complicated ways

(R)D(M)FT

The wavefunction approach

- Choose Hartree-Fock (or a small MCSCF) as the mean-field part
- Expand the exact wavefunction as a sum of many determinants
- Obtain the correlation energy using CI, PT, CC, etc. of various flavours

(R)D(M)FT

The (R)D(M)FT approach

- Choose Kohn-Sham (or similar) as the mean-field part
- Assume that the correlation energy is a functional of $\rho(\mathbf{r})$ or $\rho(\mathbf{r}, \mathbf{r}')$
- Iterate to self-consistency of some sort

(R)D(M)FT

Correlation made simple!

- Studies find that E_c depends strongly on the domain dimensionality
- Studies find that E_c depends weakly on the external potential
  - Wigner, *Trans Faraday Soc* 34 (1938) 678
  - Kohn & Sham, *Phys Rev* 140 (1965) A1133
  - Pople & Binkley, *Mol Phys* 29 (1975) 599
  - Fournais *et al.*, *Commun Math Phys* 255 (2005) 183
  - Loos & Gill, *Phys Rev Lett* 105 (2010) 113001
- E_c in complicated potentials is similar to E_c in simple potentials

$\therefore$ We can learn about E_c by studying electrons in simple potentials!

- This information can be used to construct / test new RDMFT functionals

(R)D(M)FT

So, what super-simple potential will we choose for our electrons. . . ?

Electrons on spheres

Electrons on spheres

1-sphere

Ring

n-ringium

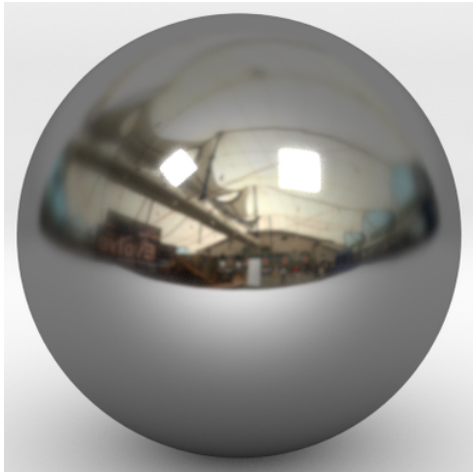
Electrons on spheres

1-sphere

Ring

n-ringium

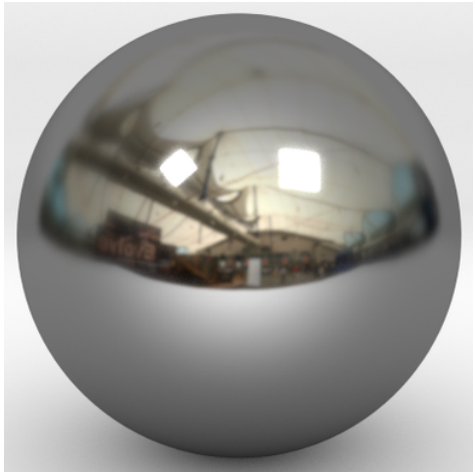
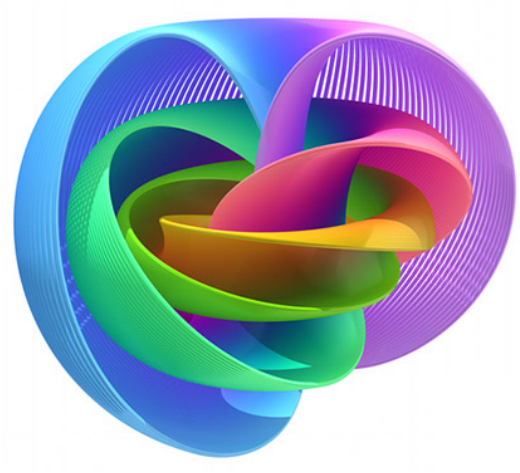
2-sphere



Normal sphere

n-spherium

Electrons on spheres

1-sphere	2-sphere	3-sphere
		
Ring	Normal sphere	Glome
n-ringium	*n*-spherium	*n*-glomium

Electrons on spheres

Making contact with the Old World

In the thermodynamic (i.e. $n \to \infty$) limit:

- the properties of n-ringium approach those of 1-jellium;
- the properties of n-spherium approach those of 2-jellium;
- the properties of n-glomium approach those of 3-jellium.

Electrons on spheres

Schrödinger equation on a sphere

- The Hamiltonian operator has only two types of term

$$\hat{\mathbf{H}} = \quad \hat{\mathbf{T}} \quad + \quad \hat{\mathbf{V}}$$

$$= -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i<j}^{n}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Let the radius of the sphere be R

$\therefore$ The kinetic energy operator $\hat{\mathbf{T}} \propto 1/R^2$ separable

$\therefore$ The potential energy operator $\hat{\mathbf{V}} \propto 1/R$ non-separable

- These different behaviours suggest two perturbative approaches ...

Perturbative approaches

The small-R and large-R regimes

$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i<j}^{n}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- $R \ll 1$: the high-density regime
  - $\hat{\mathbf{T}}$ dominates $\hat{\mathbf{V}}$. We say that the electrons are weakly correlated
  - Good starting point is a separable wavefunction
- $R \gg 1$: the low-density regime
  - $\hat{\mathbf{V}}$ dominates $\hat{\mathbf{T}}$. We say that the electrons are strongly correlated
  - Good starting point is a localized wavefunction

ELECTRONS ON SMALL SPHERES

Electrons on a small 1-sphere

An electron on a 1-sphere

1-ringium

Wavefunctions & Energies

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} \quad (r = R)$$

$$\Psi_m = \exp(\imath m \phi_1), \quad m \in \mathbb{Z}$$

$$E_m = \frac{m^2}{2R^2} \qquad (E_0 = 0)$$

Two electrons on a small 1-sphere

2-ringium

HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\Psi_{\mathrm{MF}} = \begin{vmatrix} e^{+\imath\phi_1/2} & e^{+\imath\phi_2/2} \\ e^{-\imath\phi_1/2} & e^{-\imath\phi_2/2} \end{vmatrix}$$

$$E_{\mathrm{MF}} = \frac{1}{4R^2} + \frac{2}{\pi R}$$

Two electrons on a small 1-sphere

2-ringium

Wavefunction & Energy

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\Psi = ???$$

$$E = ???$$

Two electrons on a 1-sphere

Solving the Schrödinger equation

- Changing variables to the reduced inter-electronic distance

$$x = \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{2R}$$

and separating the Schrödinger equation yields the Heun ODE

$$\left[x^2 - 1\right] \frac{d^2\psi}{dx^2} + x\frac{d\psi}{dx} + \frac{2R}{x}\psi = 4R^2\epsilon\,\psi$$

- This has polynomial solutions for particular R values, e.g.

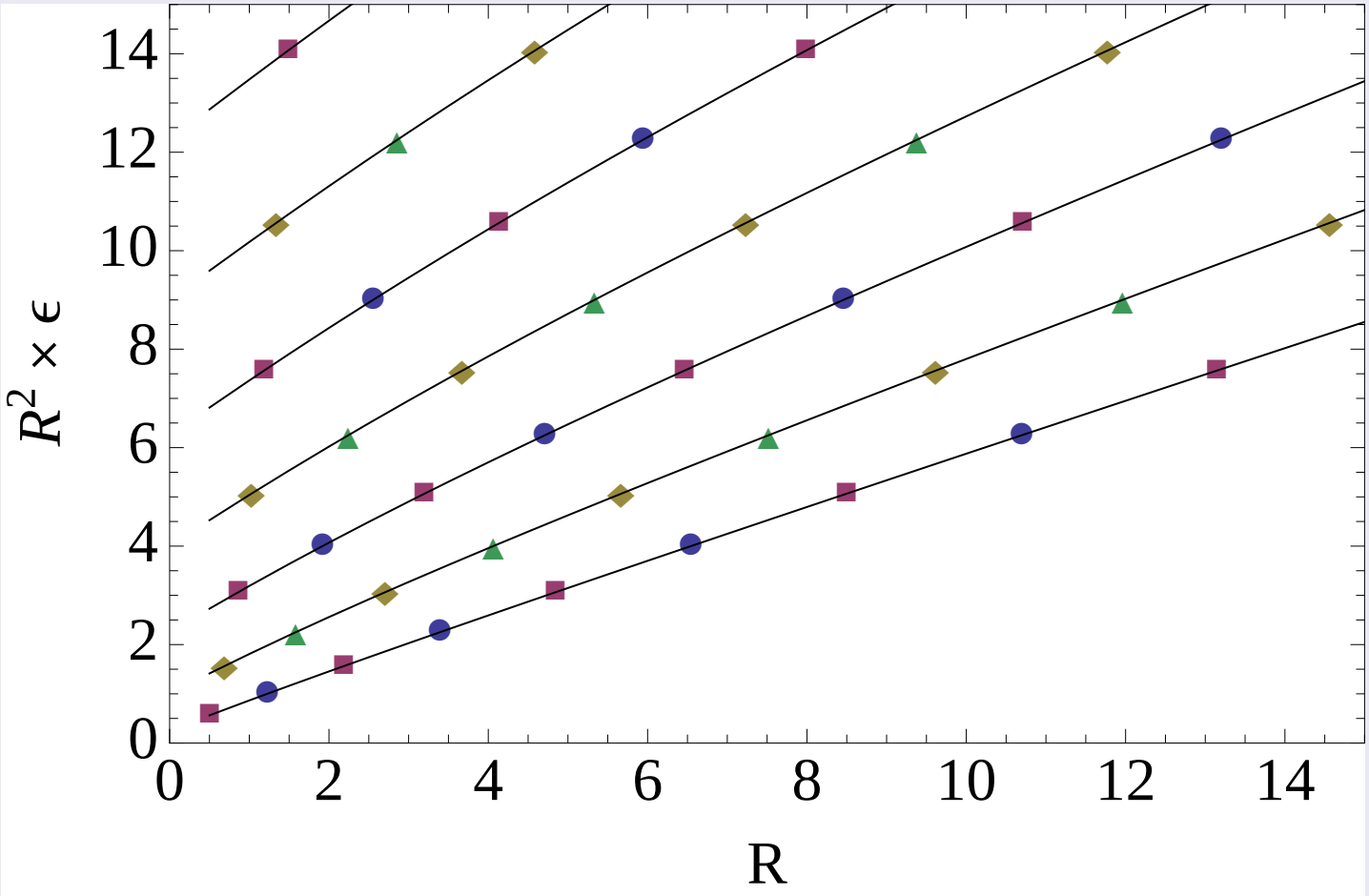
$$R = \sqrt{3/2} \qquad \epsilon = 2/3 \qquad \psi = x(1 + \sqrt{3/2}\,x)$$

$$R = \sqrt{23/2} \qquad \epsilon = 9/46 \qquad \psi = x(1 + \sqrt{23/2}\,x + 5x^2/2)$$

- There are a countably infinite number of such closed-form solutions

Two electrons on a 1-sphere

Solving the Schrödinger equation



Two electrons on a 1-sphere

PRL **108,** 083002 (2012) PHYSICAL REVIEW LETTERS week ending 24 FEBRUARY 2012

Exact Wave Functions of Two-Electron Quantum Rings

Pierre-François Loos* and Peter M. W. Gill†

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

(Received 6 December 2011; published 23 February 2012)

We demonstrate that the Schrödinger equation for two electrons on a ring, which is the usual paradigm to model quantum rings, is solvable in closed form for particular values of the radius. We show that both polynomial and irrational solutions can be found for any value of the angular momentum and that the singlet and triplet manifolds, which are degenerate, have distinct geometric phases. We also study the nodal structure associated with these two-electron states.

DOI: 10.1103/PhysRevLett.108.083002 PACS numbers: 31.15.ac, 31.15.ve, 31.15.vj, 73.21.La

Introduction.—Like quantum dots [1], quantum rings (QR) are self-organized nanometric semiconductors and are intensively studied experimentally due to their rich electronic, magnetic, and optical properties [2–7], such as the Aharonov-Bohm effect [8–10].

Many-electron QRs have been investigated theoretically using various methods, such as model Hamiltonian [11–13], exact diagonalization [14,15], quantum Monte Carlo calculations [15,16], and density-functional theory [17–20]. Accurate numerical calculations on two-electron QRs have been reported in Ref. [21].

Quantum rings are usually modeled by electrons con-

$$u = R\sqrt{2 - 2\cos(\theta_1 - \theta_2)} \tag{2}$$

is the interelectronic distance [32]. In one dimension, the singlet and triplet manifolds are degenerate [33], and this allows us to focus primarily on the singlets.

Hartree-Fock solution.—Within the Hartree-Fock (HF) approximation [35], the ground-state wave function is simply

$$\Psi_{\mathrm{HF}}(u) = u, \tag{3}$$

which has a node at $u = 0$, and the energy is

Three electrons on a small 1-sphere

3-ringium

HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{3}\nabla_i^2 + \sum_{i<j}^{3}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\mathrm{MF}} = \begin{vmatrix} e^{+\imath\phi_1} & e^{+\imath\phi_2} & e^{+\imath\phi_3} \\ e^{0\imath\phi_1} & e^{0\imath\phi_2} & e^{0\imath\phi_3} \\ e^{-\imath\phi_1} & e^{-\imath\phi_2} & e^{-\imath\phi_3} \end{vmatrix}$$

$$E_{\mathrm{MF}} = \frac{1}{R^2} + \frac{20}{3\pi R}$$

Ten electrons on a small 1-sphere

10-ringium

HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{10}\nabla_i^2 + \sum_{i<j}^{10}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\mathrm{MF}} = \det\left[e^{+\imath m\phi_j}\right]_{10\times 10}$$

$$E_{\mathrm{MF}} = \frac{165}{4R^2} + \frac{5024594}{36465\pi R}$$

n electrons on a small 1-sphere

Beyond the separable approximation

- Computing the separable energy E_{MF} is easy for any n
- Estimate the correlation energy E_c using small-R perturbation theory
- If we start from the HF wavefunction, this is Møller-Plesset theory

$$E_c = E_2 + E_3 + E_4 + \ldots$$

- For $n = 2L + 1$ electrons on a 1-sphere, one finds that

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{d_{ab}^{rs} - x_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- The ϵ_m are scaled orbital energies and are simple linear functions of R
- The d_{ab}^{rs} and x_{ab}^{rs} are four-electron integrals which are independent of R

n electrons on a small 1-sphere

The orbital energies

- The scaled orbital energies are given by

$$\epsilon_m = \frac{m^2}{2} + \frac{2R}{\pi} \sum_{a=-h}^{h} H(m-a)$$

- We have introduced the odd harmonic sum function

$$H(k) = \sum_{p=1}^{|k|} \frac{1}{2p-1}$$

- Examples: $H(0) = 0$ $H(1) = 1$ $H(2) = 4/3$ $H(3) = 23/15$

n electrons on a small 1-sphere

The four-electron integrals

- The four-electron integrals involve Chebyshev polynomials of the first kind

$$d^{rs}_{ab} = \frac{1}{\pi^4} \iiiint \frac{T_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, T_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, T_r(\mathbf{r}_1 \cdot \mathbf{r}_3)\, T_s(\mathbf{r}_2 \cdot \mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$x^{rs}_{ab} = \frac{1}{\pi^4} \iiiint \frac{T_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, T_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, T_r(\mathbf{r}_1 \cdot \mathbf{r}_4)\, T_s(\mathbf{r}_2 \cdot \mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

- They have closed forms in terms of products of the harmonic sum function

$$\begin{aligned}
(\pi^2/8) d^{rs}_{ab} &= (\delta_{r+a,s+b} + \delta_{r+a,s-b}) H(r+a)^2 \\
&\quad + (\delta_{r-a,s+b} + \delta_{r-a,s-b}) H(r-a)^2 \\
(\pi^2/8) x^{rs}_{ab} &= (\delta_{r+a,s+b} + \delta_{r+a,s-b}) H(r+a) H(s-a) \\
&\quad + (\delta_{r-a,s+b} + \delta_{r-a,s-b}) H(r-a) H(s+a)
\end{aligned}$$

- The Kronecker δ functions greatly simplify the evaluation of the E_2 sum

n electrons on a small 1-sphere

Second-order (MP2) correlation energies

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{d_{ab}^{rs} - x_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

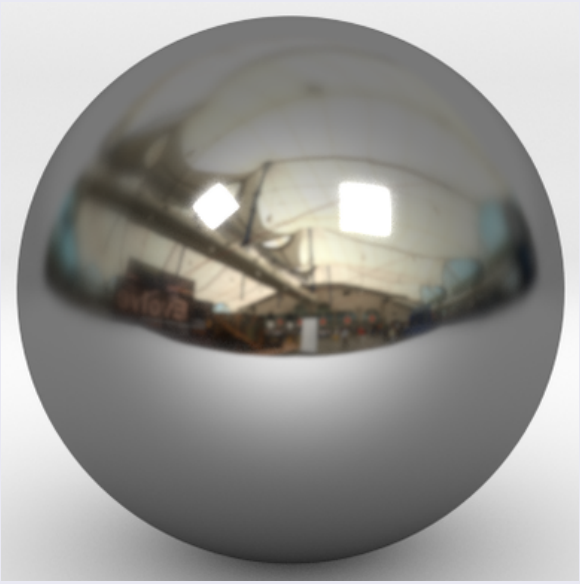
This allows us to find E_2 in closed form for any n. The values for $R = 0$ are nice...

n	E_2/n	Numerical
2	$1 - \frac{10}{\pi^2}$	–0.013 211 836
3	$\frac{16}{9} - \frac{1436}{81\pi^2}$	–0.018 484 194
4	$\frac{109}{45} - \frac{244\,168}{10\,125\pi^2}$	–0.021 174 397
⋮	⋮	⋮
∞	$-\pi^2/360$	–0.027 415 568

Electrons on a small 2-sphere

An electron on a 2-sphere

1-spherium



Wavefunctions & Energies

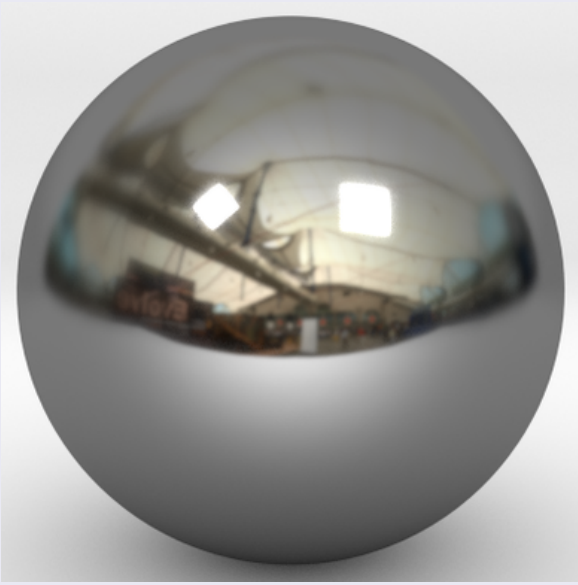
$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2}$$

$$\Psi_{lm} = Y_{lm}(\mathbf{r}_1)$$

$$E_{lm} = \frac{l(l+1)}{2R^2}$$

Two electrons on a small 2-sphere

2-spherium



HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\Psi_{\mathrm{MF}} = Y_{00}(\mathbf{r}_1)\, Y_{00}(\mathbf{r}_2)$$

$$E_{\mathrm{MF}} = \frac{0}{R^2} + \frac{1}{R}$$

Two electrons on a 2-sphere

Solving the Schrödinger equation

- Changing variables to the reduced inter-electronic distance

$$x = \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{2R}$$

and separating the Schrödinger equation yields the Heun ODE

$$\left[x^2 - 1\right] \frac{d^2\psi}{dx^2} + \left[3x - \frac{1}{x}\right] \frac{d\psi}{dx} + \frac{2R}{x}\psi = 4R^2\epsilon\,\psi$$

- This has polynomial solutions for particular R values, e.g.

$$R = \sqrt{3/4} \qquad \epsilon = 1 \qquad \psi = 1 + \sqrt{3}\,x$$

$$R = \sqrt{7} \qquad \epsilon = 2/7 \qquad \psi = 1 + \sqrt{28}\,x + 5\,x^2$$

- There are a countably infinite number of such closed-form solutions

Two electrons on a small 2-sphere

PRL **103,** 123008 (2009) PHYSICAL REVIEW LETTERS week ending 18 SEPTEMBER 2009

Two Electrons on a Hypersphere: A Quasiexactly Solvable Model

Pierre-François Loos and Peter M. W. Gill*

Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 0200, Australia

(Received 5 July 2009; published 18 September 2009)

We show that the exact wave function for two electrons, interacting through a Coulomb potential but constrained to remain on the surface of a $\mathcal{D}$-sphere ($\mathcal{D} \geq 1$), is a polynomial in the interelectronic distance u for a countably infinite set of values of the radius R. A selection of these radii and the associated energies are reported for ground and excited states on the singlet and triplet manifolds. We conclude that the $\mathcal{D} = 3$ model bears the greatest similarity to normal physical systems.

DOI: 10.1103/PhysRevLett.103.123008 PACS numbers: 31.15.ac, 31.15.ve, 31.15.vj

Quantum mechanical models for which it is possible to solve explicitly for a finite portion of the energy spectrum are said to be quasiexactly solvable [1]. They have ongoing value and are useful both for illuminating more complicated systems and for testing and developing theoretical approaches, such as density-functional theory (DFT) [2–4] and explicitly correlated methods [5–8]. One of the most famous two-body models is the Hooke's law atom, which consists of a pair of electrons repelling Coulombically but trapped in a harmonic external potential with force constant k. This system was first considered nearly 50 years ago by Kestner and Sinanoglu [9], solved analytically in

The electronic Hamiltonian, in atomic units, is

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{u}, \tag{1}$$

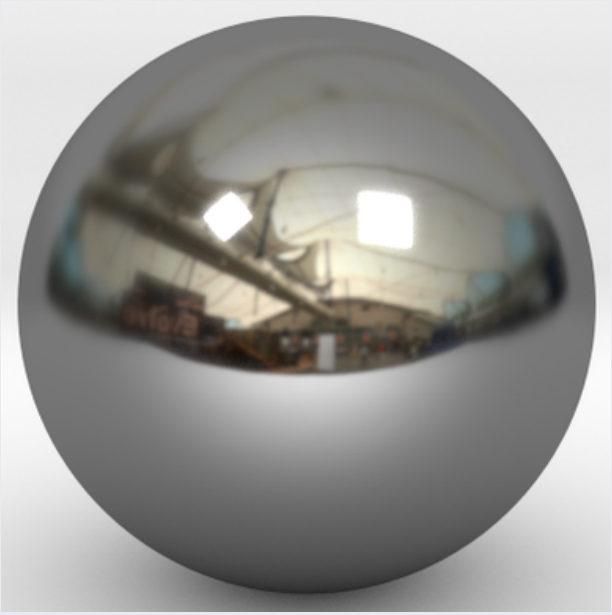
and, because each electron moves on a $\mathcal{D}$-sphere, it is natural to adopt hyperspherical coordinates [21,22].

For ^1S states, it can be then shown [19] that the wave function $S(u)$ satisfies the Schrödinger equation

$$\left[\frac{u^2}{4R^2} - 1\right]\frac{d^2S}{du^2} + \left[\frac{(2\mathcal{D}-1)u}{4R^2} - \frac{\mathcal{D}-1}{u}\right]\frac{dS}{du} + \frac{S}{u} = ES. \tag{2}$$

Four electrons on a small 2-sphere

4-spherium



HF wavefunction & energy

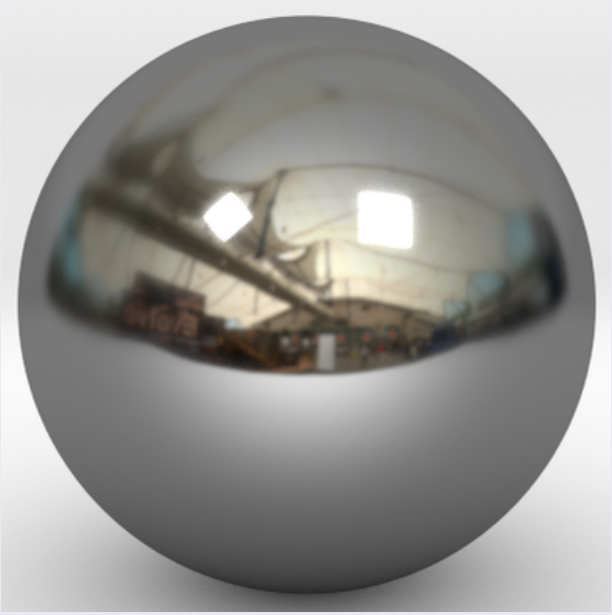
$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{4}\nabla_i^2 + \sum_{i<j}^{4}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\mathrm{MF}} = \det\left[Y_{lm}(\mathbf{r}_j)\right]_{4\times 4}$$

$$E_{\mathrm{MF}} = \frac{3}{4R^2} + \frac{11}{10R}$$

Nine electrons on a small 2-sphere

9-spherium



HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{9}\nabla_i^2 + \sum_{i<j}^{9}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\mathrm{MF}} = \det\left[Y_{lm}(\mathbf{r}_j)\right]_{9\times 9}$$

$$E_{\mathrm{MF}} = \frac{2}{R^2} + \frac{1004}{315R}$$

n electrons on a small 2-sphere

Beyond the separable approximation

- As before, computing the separable energy E_{MF} is easy for any n
- Estimate the correlation energy E_c using small-R perturbation theory
- For $n = (L+1)^2$ electrons on a 2-sphere, one finds that

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{D_{ab}^{rs} - X_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- The ϵ_m are scaled orbital energies and are simple linear functions of R
- The D_{ab}^{rs} and X_{ab}^{rs} are four-electron integrals which are independent of R

n electrons on a small 2-sphere

The four-electron integrals

- The four-electron integrals involve Legendre polynomials

$$D^{rs}_{ab} = \frac{1}{(4\pi)^4} \iiiint \frac{P_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, P_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, P_r(\mathbf{r}_1 \cdot \mathbf{r}_3)\, P_s(\mathbf{r}_2 \cdot \mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$X^{rs}_{ab} = \frac{1}{(4\pi)^4} \iiiint \frac{P_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, P_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, P_r(\mathbf{r}_1 \cdot \mathbf{r}_4)\, P_s(\mathbf{r}_2 \cdot \mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

- They usually vanish but, otherwise, they are simple rational functions, e.g.

$$D^{rs}_{01} = 3 \left[\frac{r\,\delta_{r,s+1} + s\,\delta_{r,s-1}}{(2r+1)^2} \right]$$

$$X^{rs}_{01} = 3 \left[\frac{r\,\delta_{r,s+1} + s\,\delta_{r,s-1}}{(2r+1)(2s+1)} \right]$$

- The Kronecker δ functions greatly simplify the evaluation of the E_2 sum

n electrons on a small 2-sphere

Second-order (MP2) correlation energies

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{D_{ab}^{rs} - X_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

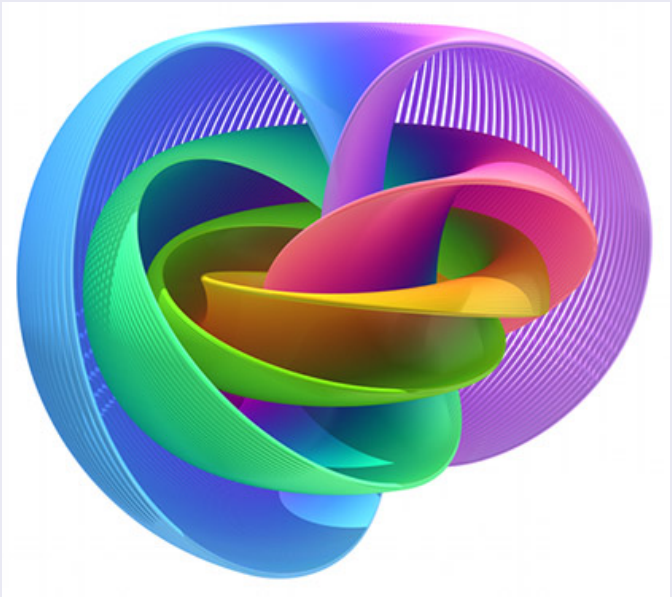
This allows us to find E_2 in closed form for several n. Here are some values for $R = 0$

n	E_2/n	Numerical
4	$\frac{98}{75} \ln 2 - \frac{691}{750}$	–0.015 621 017
9	too long to write!	–0.022 098 923
16	too long to write!	–0.025 708 123
⋮	⋮	⋮
∞	$\beta(2) - \frac{8}{\pi^2}\beta(4) + (\ln 2 - 1)/2$	–0.039 069 076

Electrons on a small 3-sphere

An electron on a 3-sphere

1-glomium



Wavefunctions & Energies

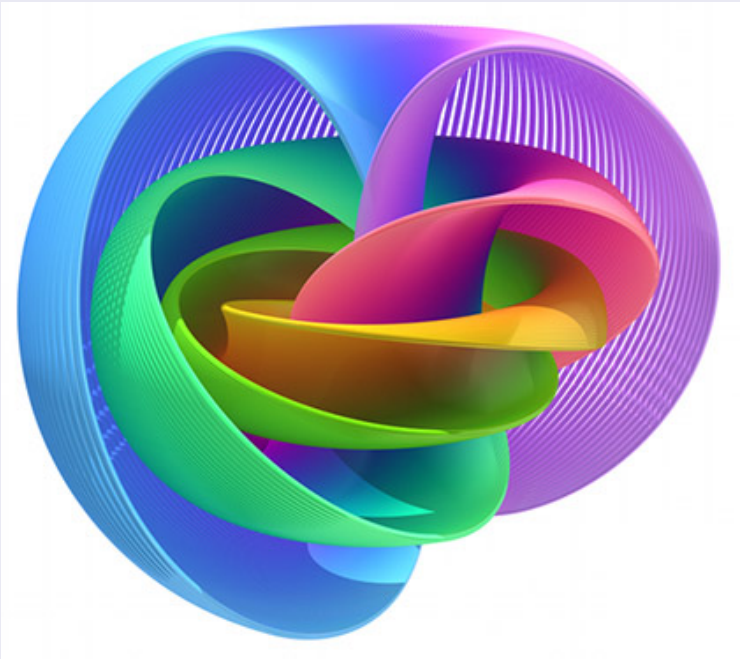
$$\hat{\mathbf{H}} = -\frac{\nabla^2}{2} \quad (r = R)$$

$$\Psi_{klm} = Y_{klm}(\mathbf{r})$$

$$E_{klm} = \frac{k(k+2)}{2R^2}$$

Two electrons on a small 3-sphere

2-glomium



HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\Psi_{\mathrm{MF}} = Y_{000}(\mathbf{r}_1)\, Y_{000}(\mathbf{r}_2)$$

$$E_{\mathrm{MF}} = \frac{0}{R^2} + \frac{8}{3\pi R}$$

Two electrons on a 3-sphere

Solving the Schrödinger equation

- Changing variables to the reduced inter-electronic distance

$$x = \frac{|\mathbf{r}_1 - \mathbf{r}_2|}{2R}$$

and separating the Schrödinger equation yields the Heun ODE

$$\left[x^2 - 1\right] \frac{d^2\psi}{dx^2} + \left[5x - \frac{2}{x}\right] \frac{d\psi}{dx} + \frac{2R}{x}\psi = 4R^2\epsilon\,\psi$$

- This has polynomial solutions for particular R values, e.g.

$$R = \sqrt{5/2} \qquad \epsilon = 1/2 \qquad \psi = 1 + \sqrt{5/2}\,x$$

$$R = \sqrt{33/2} \qquad \epsilon = 2/11 \qquad \psi = 1 + \sqrt{33/2}\,x + (7/2)x^2$$

- There are a countably infinite number of such closed-form solutions

Two electrons on a small 3-sphere

PRL **103,** 123008 (2009) PHYSICAL REVIEW LETTERS week ending 18 SEPTEMBER 2009

Two Electrons on a Hypersphere: A Quasiexactly Solvable Model

Pierre-François Loos and Peter M. W. Gill*

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(Received 5 July 2009; published 18 September 2009)

We show that the exact wave function for two electrons, interacting through a Coulomb potential but constrained to remain on the surface of a $\mathcal{D}$-sphere ($\mathcal{D} \geq 1$), is a polynomial in the interelectronic distance u for a countably infinite set of values of the radius R. A selection of these radii and the associated energies are reported for ground and excited states on the singlet and triplet manifolds. We conclude that the $\mathcal{D} = 3$ model bears the greatest similarity to normal physical systems.

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The electronic Hamiltonian, in atomic units, is

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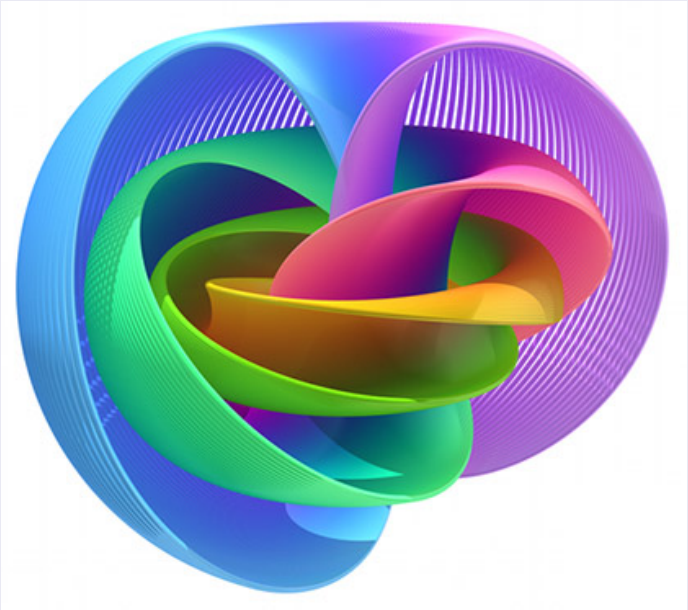
and, because each electron moves on a $\mathcal{D}$-sphere, it is natural to adopt hyperspherical coordinates [21,22].

For ^1S states, it can be then shown [19] that the wave function $S(u)$ satisfies the Schrödinger equation

$$\left[\frac{u^2}{4R^2} - 1\right]\frac{d^2S}{du^2} + \left[\frac{(2\mathcal{D}-1)u}{4R^2} - \frac{\mathcal{D}-1}{u}\right]\frac{dS}{du} + \frac{S}{u} = ES. \tag{2}$$

Fourteen electrons on a small 3-sphere

14-glomium



HF wavefunction & energy

$$\hat{\mathbf{H}} = -\frac{1}{2}\sum_{i=1}^{14}\nabla_i^2 + \sum_{i<j}^{14}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\mathrm{MF}} = \det\left[Y_{lm}(\mathbf{r}_j)\right]_{14\times 14}$$

$$E_{\mathrm{MF}} = \frac{3}{R^2} + \frac{8576}{539\pi R}$$

n electrons on a small 3-sphere

Beyond the separable approximation

- As before, computing the separable energy E_{MF} is easy for any n
- Estimate the correlation energy E_c using small-R perturbation theory
- For $n = (L+1)(L+2)(2L+3)/6$ electrons on a 3-sphere, one finds that

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{\mathcal{D}_{ab}^{rs} - \mathcal{X}_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- The ϵ_m are scaled orbital energies and are simple linear functions of R
- The $\mathcal{D}_{ab}^{rs}$ and $\mathcal{X}_{ab}^{rs}$ are four-electron integrals which are independent of R

n electrons on a small 3-sphere

The four-electron integrals

- The four-electron integrals involve Chebyshev polynomials of the second kind

$$\mathcal{D}^{rs}_{ab} = \frac{4}{\pi^2} \iiiint \frac{U_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, U_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, U_r(\mathbf{r}_1 \cdot \mathbf{r}_3)\, U_s(\mathbf{r}_2 \cdot \mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$\mathcal{X}^{rs}_{ab} = \frac{4}{\pi^2} \iiiint \frac{U_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, U_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, U_r(\mathbf{r}_1 \cdot \mathbf{r}_4)\, U_s(\mathbf{r}_2 \cdot \mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

- They usually vanish but, otherwise, they are simple rational functions, e.g.

$$\mathcal{D}^{rs}_{01} = \frac{8(r+1)(s+1)}{\pi^2} \left[\frac{\delta_{r,s+1} + \delta_{r,s-1}}{(r+\frac{1}{2})^2 (r+\frac{3}{2})^2} \right]$$

$$\mathcal{X}^{rs}_{01} = \frac{8(r+1)(s+1)}{\pi^2} \left[\frac{\delta_{r,s+1} + \delta_{r,s-1}}{(r+\frac{1}{2})(r+\frac{3}{2})(s+\frac{1}{2})(s+\frac{3}{2})} \right]$$

- The Kronecker δ functions greatly simplify the evaluation of the E_2 sum

n electrons on a small 3-sphere

Second-order (MP2) correlation energies

$$E_2 = \frac{1}{2} \sum_{a=0}^{L} \sum_{b=0}^{L} \sum_{r=L+1}^{\infty} \sum_{s=L+1}^{\infty} \frac{\mathcal{D}_{ab}^{rs} - \mathcal{X}_{ab}^{rs}}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

This allows us to find E_2 in closed form for several n. The values for $R = 0$ are nice...

n	E_2/n	Numerical
5	$\frac{2248}{1575} - \frac{246805504}{17364375\pi^2}$	–0.012 809 318
14	too long to write!	–0.021 710 394
30	too long to write!	–0.028 625 250
⋮	⋮	⋮
∞	$-\infty$	$-\infty$

ELECTRONS ON LARGE SPHERES

Electrons on a large spheres

Electrons at low densities

- At low densities, $\hat{\mathbf{V}}$ dominates $\hat{\mathbf{T}}$.
  - Two electrons on a sphere form a Wigner molecule
  - The electrons localize near antipodal positions
  - $\psi(x)$ peaks strongly near $x = 1$, i.e. near $|\mathbf{r}_1 - \mathbf{r}_2| = 2R$
- Wigner molecules also form for $n > 2$ electrons
  - The electrons localize, forming a lattice
  - In 1D, the lattice points are uniformly distributed around the ring
  - In 2D, the lattice points solve the n-particle Thomson problem
  - In 3D, the lattice points solve the Thomson problem on a glome

Electrons on a large 1-sphere

Two electrons on a large 1-sphere

PRL **108,** 083002 (2012) PHYSICAL REVIEW LETTERS week ending 24 FEBRUARY 2012

Exact Wave Functions of Two-Electron Quantum Rings

Pierre-François Loos* and Peter M. W. Gill†

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

(Received 6 December 2011; published 23 February 2012)

We demonstrate that the Schrödinger equation for two electrons on a ring, which is the usual paradigm to model quantum rings, is solvable in closed form for particular values of the radius. We show that both polynomial and irrational solutions can be found for any value of the angular momentum and that the singlet and triplet manifolds, which are degenerate, have distinct geometric phases. We also study the nodal structure associated with these two-electron states.

DOI: 10.1103/PhysRevLett.108.083002 PACS numbers: 31.15.ac, 31.15.ve, 31.15.vj, 73.21.La

Introduction.—Like quantum dots [1], quantum rings (QR) are self-organized nanometric semiconductors and are intensively studied experimentally due to their rich electronic, magnetic, and optical properties [2–7], such as the Aharonov-Bohm effect [8–10].

Many-electron QRs have been investigated theoretically using various methods, such as model Hamiltonian [11–13], exact diagonalization [14,15], quantum Monte Carlo calculations [15,16], and density-functional theory [17–20]. Accurate numerical calculations on two-electron QRs have been reported in Ref. [21].

Quantum rings are usually modeled by electrons con-

$$u = R\sqrt{2 - 2\cos(\theta_1 - \theta_2)} \tag{2}$$

is the interelectronic distance [32]. In one dimension, the singlet and triplet manifolds are degenerate [33], and this allows us to focus primarily on the singlets.

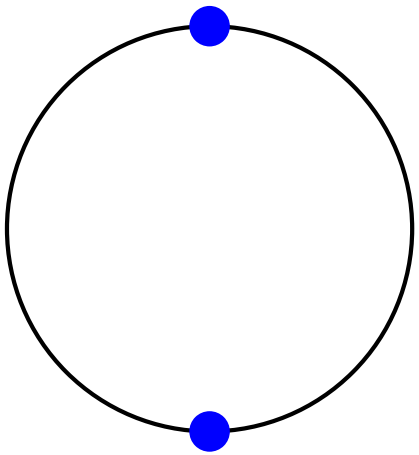
Hartree-Fock solution.—Within the Hartree-Fock (HF) approximation [35], the ground-state wave function is simply

$$\Psi_{\mathrm{HF}}(u) = u, \tag{3}$$

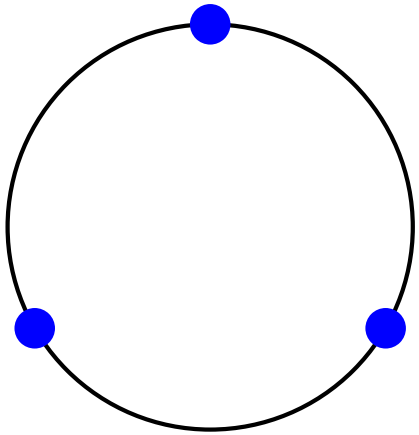
which has a node at $u = 0$, and the energy is

n electrons on a large 1-sphere

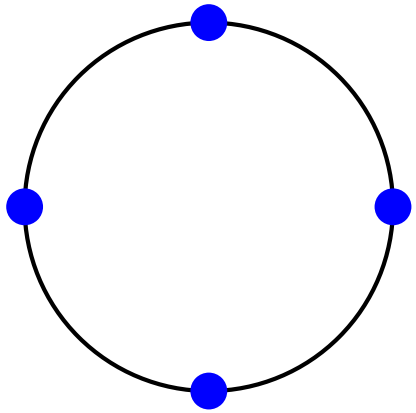
Low-density limit of 2-, 3-, 4- and 5-ringium



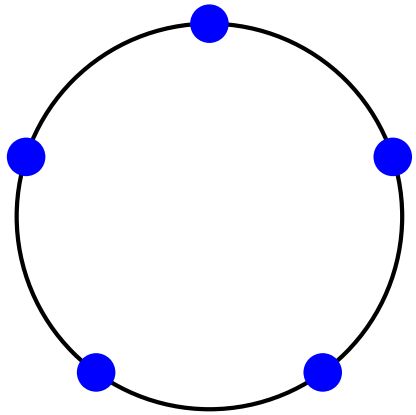
2-ringium



3-ringium

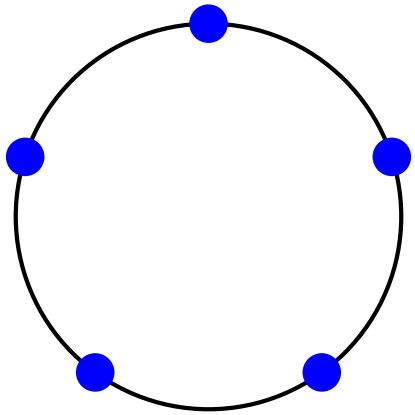


4-ringium



5-ringium

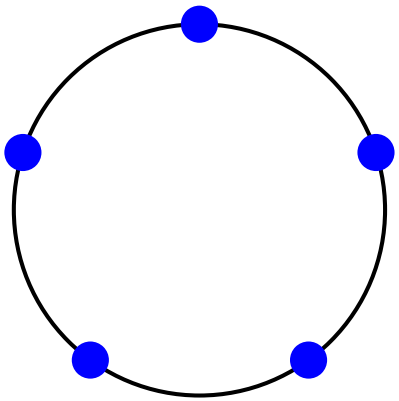
n electrons on a large 1-sphere



Low-density wavefunctions

- As $R \to \infty$, the wavefunction Ψ reduces to a sum of Dirac δ functions
- What is a good approximate Ψ when R is large but not infinite?
- We need to choose an approximation that leads to tractable integrals

n electrons on a large 1-sphere



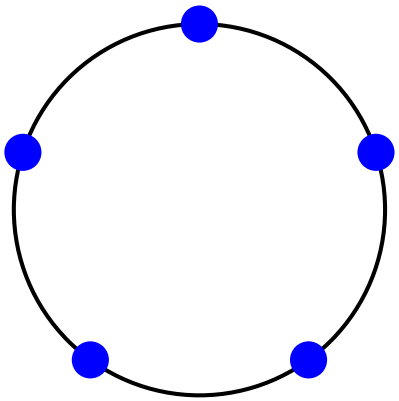
An approximate low-density wavefunction

- We have explored the usefulness of

$$\Psi = \Psi_{\mathrm{MF}} \prod_{i<j}^{n} |\mathbf{r}_i - \mathbf{r}_j|^p$$

  where p is variationally optimized
- As $p \to 0$, this reduces to the Ψ_{MF} wavefunction
- As $p \to \infty$, this yields the "Dirac δ" wavefunction
- We find that the optimal power $p \approx \sqrt{R}$

n electrons on a large 1-sphere



Many-electron Integrals

- We seek the energy of the approximate wavefunction

$$\Psi = \Psi_{\mathrm{MF}} \prod_{i<j}^{n} |\mathbf{r}_i - \mathbf{r}_j|^p$$

- This requires overlap, kinetic and coulomb integrals

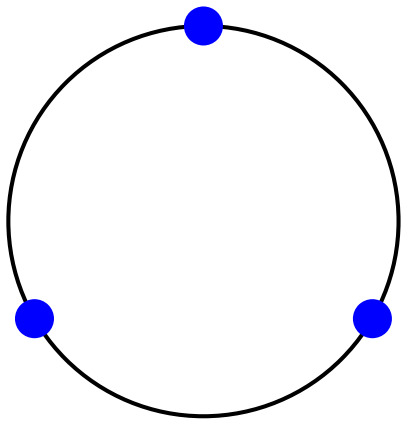
$${}_1S_n(p) = \int \ldots \int \Psi^* \Psi \; d\mathbf{r}_1 \ldots d\mathbf{r}_n$$

$${}_1T_n(p) = \int \ldots \int \Psi^* \left[-\frac{\nabla^2}{2} \right] \Psi \; d\mathbf{r}_1 \ldots d\mathbf{r}_n$$

$${}_1V_n(p) = \frac{n(n-1)}{2} \int \ldots \int \frac{\Psi^* \Psi}{|\mathbf{r}_1 - \mathbf{r}_2|} \; d\mathbf{r}_1 \ldots d\mathbf{r}_n$$

on the unit 1-sphere

n electrons on a large 1-sphere



Integral formulae for 3-ringium

$$ {}_1S_3(p) = \frac{\Gamma(3p+1)}{\Gamma(p+1)^3} $$

$$ {}_1T_3(p) = \frac{\Gamma(3p+1)}{\Gamma(p+1)^3}\,\frac{p^2}{(2p-1)} $$

$$ {}_1V_3(p) = \frac{3\;4^{2p}}{2\pi p}\,\frac{\Gamma(p+\frac{1}{2})\Gamma(3p+\frac{1}{2})}{\Gamma(2p+\frac{1}{2})^2} $$

Electrons on a large 2-sphere

Two electrons on a large 2-sphere

PRL **103,** 123008 (2009) PHYSICAL REVIEW LETTERS week ending 18 SEPTEMBER 2009

Two Electrons on a Hypersphere: A Quasiexactly Solvable Model

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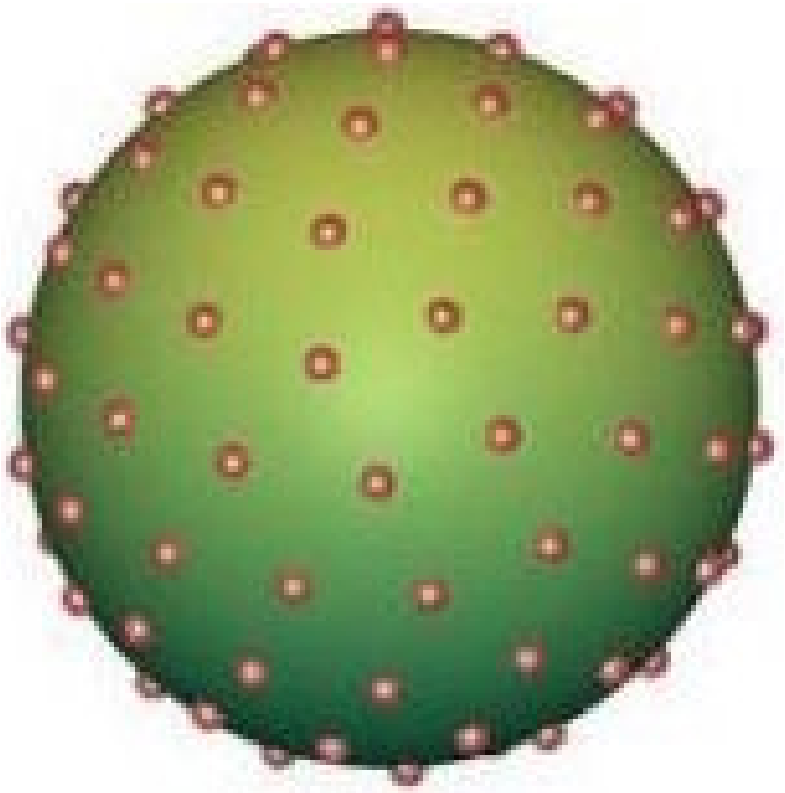
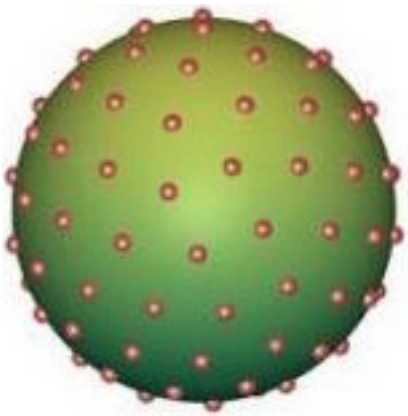
Electrons on a large 2-sphere

Low-density limit of 100-spherium



n electrons on a large 2-sphere



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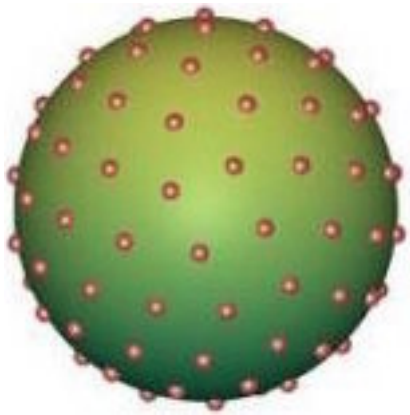

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Electrons on a large 3-sphere

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Electrons on a large 3-sphere

THE JOURNAL OF CHEMICAL PHYSICS **143**, 084114 (2015)

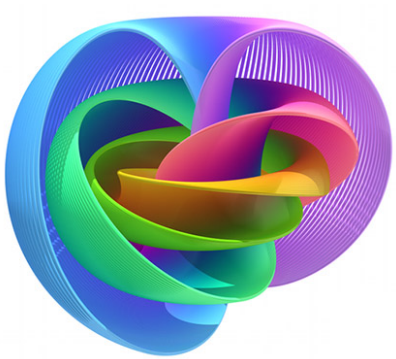
Uniform electron gases. III. Low-density gases on three-dimensional spheres

Davids Agboola, Anneke L. Knol, Peter M. W. Gill,[a] and Pierre-François Loos[b]
Research School of Chemistry, Australian National University, Canberra ACT 2601, Australia

(Received 23 June 2015; accepted 10 August 2015; published online 25 August 2015)

By combining variational Monte Carlo (VMC) and complete-basis-set limit Hartree-Fock (HF) calculations, we have obtained near-exact correlation energies for low-density same-spin electrons on a three-dimensional sphere (3-sphere), i.e., the surface of a four-dimensional ball. In the VMC calculations, we compare the efficacies of two types of one-electron basis functions for these strongly correlated systems and analyze the energy convergence with respect to the quality of the Jastrow factor. The HF calculations employ spherical Gaussian functions (SGFs) which are the curved-space analogs of Cartesian Gaussian functions. At low densities, the electrons become relatively localized into Wigner crystals, and the natural SGF centers are found by solving the Thomson problem (i.e., the minimum-energy arrangement of n point charges) on the 3-sphere for various values of n. We have found 11 special values of n whose Thomson sites are equivalent. Three of these are the vertices of four-dimensional Platonic solids — the hyper-tetrahedron ($n = 5$), the hyper-octahedron ($n = 8$), and the 24-cell ($n = 24$) — and a fourth is a highly symmetric structure ($n = 13$) which has not previously been reported. By calculating the harmonic frequencies of the electrons around their equilibrium positions, we also find the first-order vibrational corrections to the Thomson energy. [http://dx.doi.org/10.1063/1.4929353]

n electrons on a large 3-sphere



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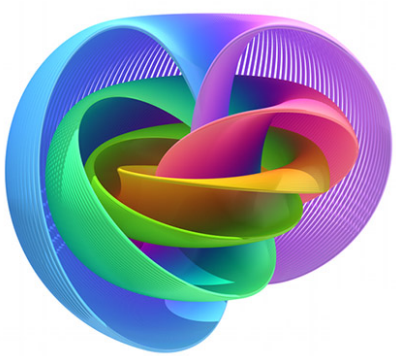

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on the unit 3-sphere

SUMMARY

Concluding Remarks

In a nutshell . . .

- The electron correlation problem lies at the heart of RDMFT theory
- Fortunately, much can be learned by studying electrons on D-spheres
- For high electron densities, interesting four-electron integrals arise

  These are solved in 1D, but many remain unsolved in 2D and 3D
- For low electron densities, fascinating many-electron integrals arise

  Special cases are solved, but the general cases remain unsolved

The Challenges . . .

The four-electron integrals on the D-sphere

$$X_{ab}^{rs} = \frac{1}{(4\pi)^4} \iiiint \frac{P_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, P_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, P_r(\mathbf{r}_1 \cdot \mathbf{r}_4)\, P_s(\mathbf{r}_2 \cdot \mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

$$\mathcal{X}_{ab}^{rs} = \frac{4}{\pi^2} \iiiint \frac{U_a(\mathbf{r}_1 \cdot \mathbf{r}_3)\, U_b(\mathbf{r}_2 \cdot \mathbf{r}_4)\, U_r(\mathbf{r}_1 \cdot \mathbf{r}_4)\, U_s(\mathbf{r}_2 \cdot \mathbf{r}_3)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4$$

The many-electron integrals on the D-sphere

$$S_n(p) = \int \ldots \int \Psi^* \Psi \; d\mathbf{r}_1 \ldots d\mathbf{r}_n$$

$$T_n(p) = \int \ldots \int \Psi^* \left[-\frac{\nabla^2}{2} \right] \Psi \; d\mathbf{r}_1 \ldots d\mathbf{r}_n$$

$$V_n(p) = \frac{n(n-1)}{2} \int \ldots \int \frac{\Psi^* \Psi}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1 \ldots d\mathbf{r}_n$$