

Finite Uniform Electron Gases (FUEGs)

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My FUEG Collaborators

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1995 – now

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2008 – 2017

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2019 – 2021

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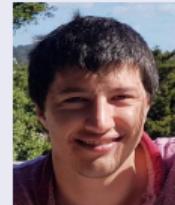
2014 – 2015

Simon McKenzie



2015 – 2021

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2016 – 2018

Outline

1 Background

- The Correlation Problem
- Electrons on a sphere
- Orbitals on a sphere

2 (1,1)-spherium

- Hartree-Fock
- Exact
- Higher states

3 (n,0)-spherium

- Hartree-Fock
- Configuration Interaction
- Configuration State Functions

Background

(1,1)-spherium

(n,0)-spherium

The Correlation Problem

Electrons on a sphere

Orbitals on a sphere

Background

The Electron Correlation Problem

In a nutshell...

- 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), ...

- We are interested in the lowest few eigenvalues (energies) E
- We usually split the energy into “mean-field” and “non-mean-field” parts

$$E = E_{\text{HF}} + E_c$$

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

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

The Electron Correlation Problem

Correlation made simple!

- Studies find that $E_c[\rho]$ depends **strongly** on the domain dimensionality
- Studies find that $E_c[\rho]$ 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
- $E_c[\rho]$ in complicated potentials is similar to $E_c[\rho]$ in simple potentials
 - ∴ We can learn about E_c by studying electrons in simple potentials!
 - So, what **super-simple potential** will we choose for our electrons...?

Electrons on a sphere

The Hamiltonian

- The Hamiltonian operator has only two types of term

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

- If the radius of the sphere is R , then

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

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

- These different behaviours suggest two perturbative approaches ...

Electrons on a sphere

Perturbative approaches

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

- $R \ll 1$: 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 a sphere

What spheres am I considering?

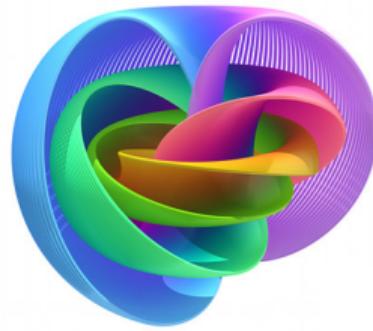
1-sphere



2-sphere



3-sphere



Ring

(n_α, n_β) -ringium

Normal sphere

(n_α, n_β) -spherium

Glome

(n_α, n_β) -glomium

Electrons on a sphere

But, because time is short today...

2-sphere



Normal sphere

(n_α, n_β) -spherium

Orbitals on a 2-sphere

(1,0)-spherium



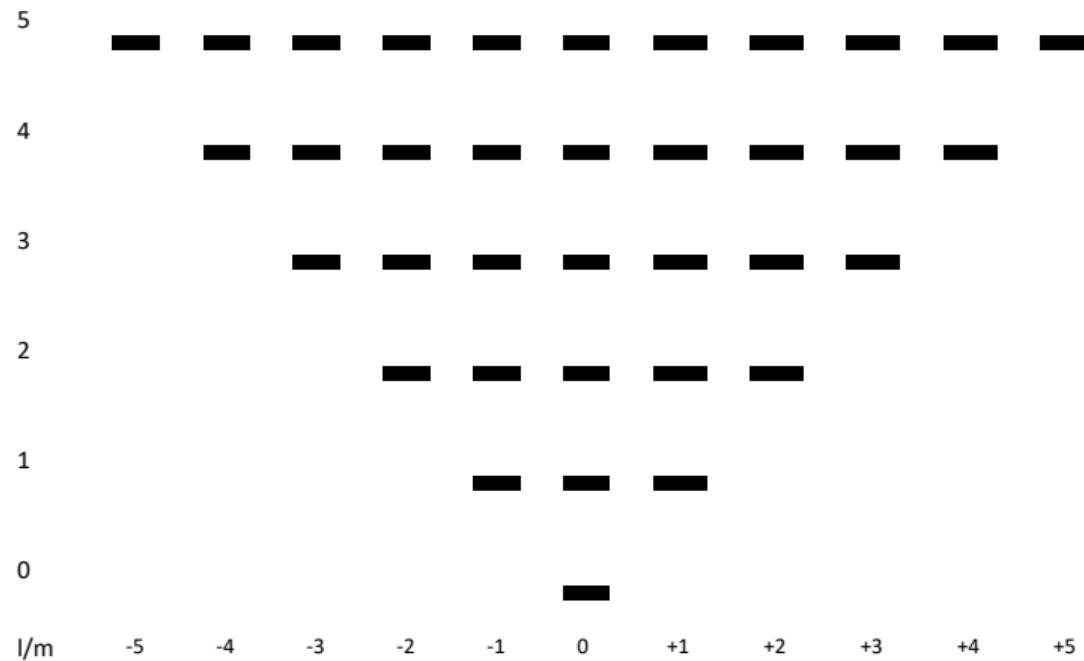
Wavefunctions & Energies

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

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

$$E_{\ell m} = \frac{\ell(\ell+1)}{2R^2}$$

Orbital energies on a 2-sphere



Background
(1,1)-spherium
(n,0)-spherium

Hartree-Fock
Exact
Higher states

(1,1)-spherium

Background
(1,1)-spherium
(n,0)-spherium

Hartree-Fock
Exact
Higher states

Hartree-Fock ground state for (1,1)-spherium

(1,1)-spherium



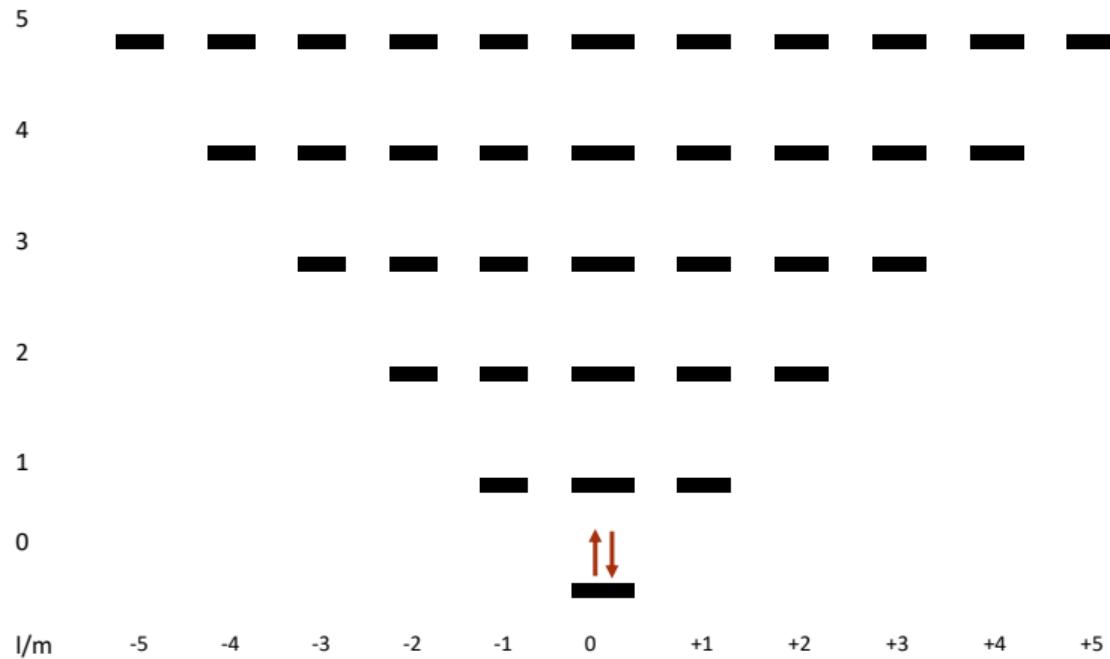
HF wavefunction & energy

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

$$\Psi_{\text{HF}} = Y_{00}(\mathbf{r}_1) Y_{00}(\mathbf{r}_2)$$

$$E_{\text{HF}} = \frac{0}{R^2} + \frac{1}{R}$$

HF for (1,1)-spherium



Background
(1,1)-spherium
(n,0)-spherium

Hartree-Fock
Exact
Higher states

Exact ground state for (1,1)-spherium

(1,1)-spherium



Wavefunction & Energy

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

$$\Psi = ???$$

$$E = ???$$

Exact ground state for (1,1)-spherium

Solving the Schrödinger equation

- Changing variables to the reduced inter-electronic distance $x = |\mathbf{r}_1 - \mathbf{r}_2|/(2R)$ and separating the Schrödinger equation yields, for 1S states, 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.

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

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

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

Exact excited states for (1,1)-spherium

Solving the Schrödinger equation

- Changing variables to the reduced inter-electronic distance $x = |\mathbf{r}_1 - \mathbf{r}_2|/(2R)$ and separating the Schrödinger equation yields, for 3P states, the Heun ODE

$$\left[x^2 - 1\right] \frac{d^2\psi}{dx^2} + \left[5x - \frac{3}{x}\right] \frac{d\psi}{dx} + \frac{2R}{x}\psi = 4R^2\epsilon\psi$$

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

$$R = \sqrt{15/4} \quad \epsilon = 1/3 \quad \psi = 1 + \sqrt{5/3}x$$

$$R = \sqrt{23} \quad \epsilon = 3/23 \quad \psi = 1 + 2\sqrt{23}/3x + 7/3x^2$$

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

Two electrons on a sphere

Extensions

- The same approach works for states of other **symmetry**
For example, 1P , 1D , 3D , 1F , 3F , etc.
- The same approach works for spheres of other **dimension**
For example, (1,1)-ringium, (1,1)-glomium, etc.
- In all cases, **exact polynomial solutions** exist for certain R
- In some cases, **exact irrational solutions** exist for certain R
- These solutions provide **benchmarks** for approximate methods

Two electrons on a sphere

PRL 103, 123008 (2009)

PHYSICAL REVIEW LETTERS

week ending
18 SEPTEMBER 2009

Two Electrons on a Hypersphere: A Quasixactly Solvable Model

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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.

DOI: 10.1103/PhysRevLett.103.123008

PACS numbers: 31.15.ac, 31.15.vc, 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 quasixactly 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

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

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

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

Two electrons on a sphere

Molecular Physics
Vol. 108, Nos. 19–20, 10–20 October 2010, 2527–2532



INVITED ARTICLE Excited states of spherium

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(Received 21 April 2010; final version received 8 July 2010)

We report analytic solutions of a recently discovered quasi-exactly solvable model consisting of two electrons, interacting via a Coulomb potential, but restricted to remain on the surface of a \mathcal{D} -dimensional sphere. Polynomial solutions are found for the ground state, and for some higher ($L \leq 3$) states. Kato cusp conditions and interdimensional degeneracies are discussed.

Keywords: exact solution; excited states; spherium; cusp condition; interdimensional degeneracies

1. Introduction

A quasi-exactly solvable model is one for which it is possible to solve the Schrödinger equation exactly for a finite portion of the energy spectrum [1]. In quantum chemistry, a famous example of this is the Hooke's law atom [2–5], which consists of a pair of electrons, repelling Coulombically but trapped in a harmonic external potential. This model and others [6–12] have been used extensively to test various approximations [13–20] within density functional theory (DFT) [21–23] and explicitly correlated methods [24–28].

2. Wave function

The Hamiltonian of \mathcal{D} -spherium is

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

where the two first terms represent the kinetic contribution of each electron, and u^{-1} is the Coulomb operator.

Following Breit [38], we write the total wave function as the product

$$\Phi([s_1, s_2], [\Omega_1, \Omega_2], u) = \Xi(s_1, s_2)\chi(\Omega_1, \Omega_2)\Psi(u), \quad (2)$$

where Ξ , χ , and Ψ are the spin, angular, and

Two electrons on a sphere

PRL 108, 083002 (2012)

PHYSICAL REVIEW LETTERS

week ending
24 FEBRUARY 2012

Exact Wave Functions of Two-Electron Quantum Rings

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(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 confined to a strict- or quasi-one-dimensional circular space interacting via a short-ranged or Coulomb operator. In this

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

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

$$\Psi_{\text{HF}}(u) = u, \quad (3)$$

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

$$\epsilon_{\text{HF}} = \frac{1}{4R^2} + \frac{2}{\pi R}. \quad (4)$$

More than two electrons on a sphere

The Three-Body Problem

- Unfortunately, we find no such exact solutions for three electrons
- The Hamiltonian is

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{\nabla_3^2}{2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|}$$

but our attempts to find a helpful change of variables have failed

- Can it be proven that no polynomial or irrational solutions exist?
- (n_α, n_β) -spherium with $n_\alpha, n_\beta > 1$ is nonetheless interesting
- Many such systems are finite uniform electron gases (FUEGs)
- Time is short, so I will discuss only $(n_\alpha, 0)$ -spherium today...

(n,0)-spherium

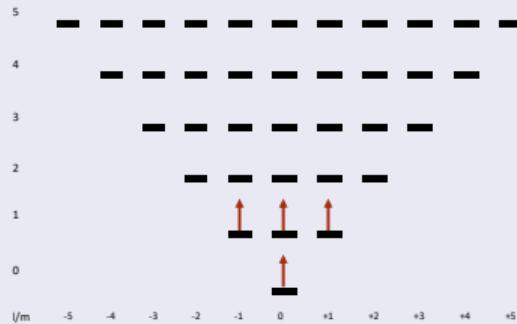
Hartree-Fock for $(n, 0)$ -spherium

Finite Uniform Electron Gases (FUEGs)

- We are particularly interested in systems with uniform densities
- We therefore focus on systems with (half-) filled shells
- To fill all orbitals with $\ell \leq h$, we require $n = (h + 1)^2$ electrons
- Thus, we consider (1,0)-, (4,0)-, (9,0)-, (16,0)-spherium, etc.

(4,0)-spherium

HF occupied orbitals ($h = 1$)



HF wavefunction & energy

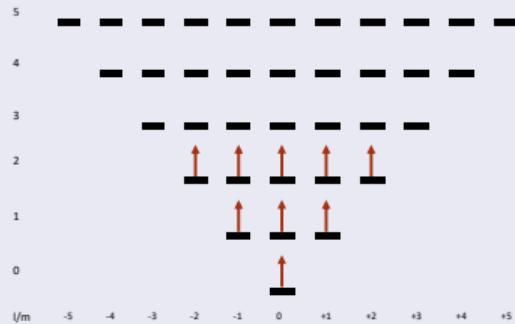
$$\hat{H} = -\frac{1}{2} \sum_{i=1}^4 \nabla_i^2 + \sum_{i < j}^4 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\text{HF}} = \det [Y_{\ell m}(\mathbf{r}_j)]_{4 \times 4}$$

$$E_{\text{HF}} = \frac{3}{4R^2} + \frac{11}{10R}$$

(9,0)-spherium

HF occupied orbitals ($h = 2$)



HF wavefunction & energy

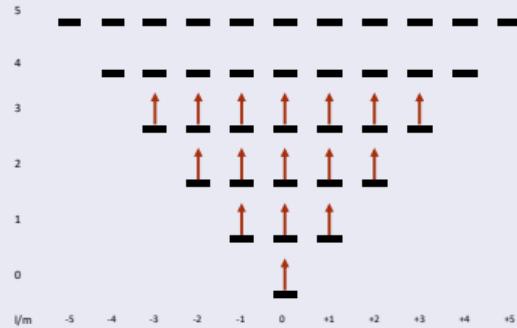
$$\hat{H} = -\frac{1}{2} \sum_{i=1}^9 \nabla_i^2 + \sum_{i < j}^9 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\text{HF}} = \det [Y_{\ell m}(\mathbf{r}_j)]_{9 \times 9}$$

$$E_{\text{HF}} = \frac{2}{R^2} + \frac{1004}{315R}$$

(16,0)-spherium

HF occupied orbitals ($h = 3$)



HF wavefunction & energy

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{16} \nabla_i^2 + \sum_{i < j}^{16} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi_{\text{HF}} = \det [Y_{\ell m}(\mathbf{r}_j)]_{16 \times 16}$$

$$E_{\text{HF}} = \frac{15}{4R^2} + \frac{37657}{6006R}$$

Configuration Interaction for $(n, 0)$ -spherium

Approximating the exact many-electron wavefunction

- Computing the Hartree-Fock energy E_{HF} is easy for any h
- But how can we estimate the correlation energy E_c ?
- Obvious approach is to admix all possible substituted determinants

$$\Psi = \Psi_{\text{HF}} + \sum_{\substack{r \in \text{virt} \\ a \in \text{occ}}} c_a^r \Psi_a^r + \sum_{\substack{rs \in \text{virt} \\ ab \in \text{occ}}} c_{ab}^{rs} \Psi_{ab}^{rs} + \sum_{\substack{rst \in \text{virt} \\ abc \in \text{occ}}} c_{abc}^{rst} \Psi_{abc}^{rst} + \dots$$

- None of the Ψ_a^r determinants mix with Ψ_{HF} so simplest approximation is

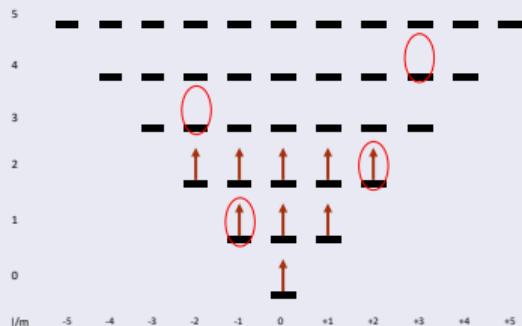
$$\Psi_{\text{CID}} = \Psi_{\text{HF}} + \sum_{\substack{rs \in \text{virt} \\ ab \in \text{occ}}} c_{ab}^{rs} \Psi_{ab}^{rs}$$

- However, the number of Ψ_{ab}^{rs} determinants can be impractically large...

CID for (9, 0)-spherium using orbitals up to $L = 4$

Consider $pd \rightarrow fg$ double substitutions

HF occupied orbitals ($h = 2$)



The determinant explosion

- $3 \times 5 = 15$ pd choices
- $7 \times 9 = 63$ fg choices
- $15 \times 63 = 945$ determinants (!)
Conserve $M = m_1 + m_2 \Rightarrow 97$ dets
There are too many determinants
- Are we fully exploiting symmetry?
Definitely not. But who can help us?

Two Masters of Invariants



Alfred Clebsch (1833 – 1872)

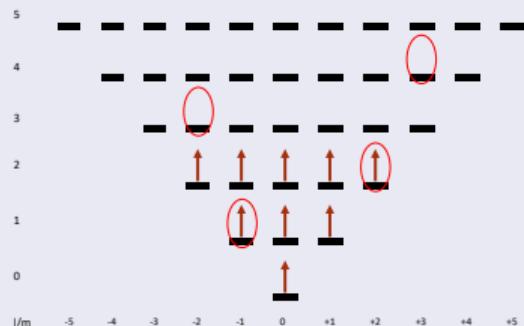


Paul Gordan (1837 – 1912)

The Key Solution

Consider $pd \rightarrow fg$ double substitutions

HF occupied orbitals ($h = 2$)



Clebsch-Gordan invariants

- $P \otimes D = P \oplus D \oplus F$
 $3 \times 5 = 3 + 5 + 7$
- $F \otimes G = P \oplus D \oplus F \oplus G \oplus H \oplus I \oplus K$
 $7 \times 9 = 3 + 5 + 7 + 9 + 11 + 13 + 15$
- CSFs? $P \leftrightarrow P$, $D \leftrightarrow D$ and $F \leftrightarrow F$
- Adds only 3 terms to CI expansion
- Now we are exploiting symmetry!

Cheap CI calculations

Size of the CI matrices for (4,0)-spherium

L	CISD		CISDT		CISDTQ	
	Determinants	CSFs	Determinants	CSFs	Determinants	CSFs
1	1	1	1	1	1	1
2	61	2	41	3	6	3
3	397	4	881	9	496	11
4	1 261	6	5 321	19	5 986	29
5	2 977	8	19 841	35	35 961	66
6	5 941	10	56 761	57	148 996	136
7	10 621	12	136 881	87	487 636	257
8	17 557	14	292 601	125	1 353 276	450
9	27 361	16	571 521	173	3 321 961	751
10	40 717	18	1 040 521	231	7 413 706	1 193
11	58 381	20	1 790 321	301	15 329 616	1 824
12	81 181	22	2 940 521	383	29 772 766	2 701
13	110 017	24	4 645 121	479	54 870 481	3 889
14	145 861	26	7 098 521	589	96 717 336	5 460

Cheap CI calculations

Size of the CI matrices for (9,0)-spherium

L	CISD		CISDT		CISDTQ	
	Determinants	CSFs	Determinants	CSFs	Determinants	CSFs
2	1	1	1	1	1	1
3	757	4	2941	12	4411	21
4	4321	11	47041	71	229321	277
5	12637	20	245701	209	2211301	1410
6	28081	30	829921	466	11515141	4651
7	53461	40	2203741	859	42972931	11859
8	92017	50	5009761	1428	129627541	25690
9	147421	60	10204741	2178	336756421	49602
10	223777	70	19145281	3151	782563321	88065
11	325621	80	33683581	4345	1667337211	146536
12	457921	90	56273281	5806	3313089361	231704
13	626077	100	90085381	7528	6215891221	351437
14	835921	110	139134241	9561	11113347421	515057
15	1093717	120	208413661	11895	19069849891	733260

Cheap CISD calculations

Reduced CISD correlation energies (mE_h) for $r_s = 1$

L	N	(4,0)	(9,0)	(16,0)	(25,0)
4	25	-13.077 115	-14.438 486	- 8.806 632	- 0.000 000
8	81	-13.289 706	-17.119 196	-17.973 776	-16.775 979
16	289	-13.306 860	-17.254 243	-18.586 734	-18.819 193
32	1 089	-13.308 117	-17.262 700	-18.617 592	-18.903 864
64	4 225	-13.308 203	-17.263 243	-18.619 453	-18.908 623
128	16 641	-13.308 208	-17.263 277	-18.619 569	-18.908 912
256	66 049	-13.308 209	-17.263 280	-18.619 576	-18.908 930
512	263 169	-13.308 209	-17.263 280	-18.619 577	-18.908 931
1024	1 050 625	-13.308 209	-17.263 280	-18.619 577	-18.908 931
∞	∞	-13.308 209	-17.263 280	-18.619 577	-18.908 931

Concluding Remarks

In a nutshell . . .

- Electrons confined to \mathcal{D} -spheres often form finite uniform electron gases
- The Schrödinger eqn is exactly solvable for two electrons on a \mathcal{D} -sphere
 - Many of the exact wavefunctions are polynomials in $|\mathbf{r}_1 - \mathbf{r}_2|$
 - These solutions are useful benchmarks for approximate methods
- For many electrons on a sphere, Ψ_{HF} and E_{HF} are easy to compute
 - The use of Configuration State Functions permits huge CID calculations

Low-density electrons on a 3-sphere

THE JOURNAL OF CHEMICAL PHYSICS 143, 084114 (2015)

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

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(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. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929353>]