

Nodal Surfaces in Quasi-Exactly Solvable Models

Pierre-François Loos,¹ Peter Gill,¹ and Dario Bressanini²

¹Research School of Chemistry, Australian National University, Canberra, Australia

²Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Como, Italy



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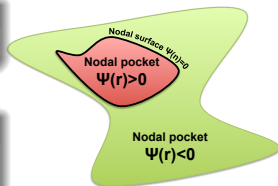
Nodes, Nodal Pockets and Fixed-Node Approximation

What's a node?

node = point in **configuration space** n for which $\Psi(n) = 0$

What's a nodal pocket?

nodal pocket = region of **configuration space** in which electrons can travel **without** crossing a node



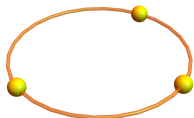
Why is it important to know the nodes?

- ☹ Vanilla **DMC** algorithm converges to **bosonic** ground state
- 😊 Nodes of the **trial** wave function has to be fixed: **fixed-node (FN) approximation**
- ☹ FN-DMC gives **exact** energy **iff** the nodes are **exact**
- 😊 FN **error** proportional to the **square** of the node displacement
- ☹ FN **error** very hard to **estimate**
- ☹ Nodes poorly understood due to **high** dimensionality of nodal **hypersurface**

Ceperley, J Phys Stat 63 (1991) 1237

Electrons on a Ring

Where are the nodes?



... when 2 electrons touch! (Pauli nodes)

$$\Psi_0^{1D} = \begin{vmatrix} e^{-i\phi_1} & 1 & e^{+i\phi_1} \\ e^{-i\phi_2} & 1 & e^{+i\phi_2} \\ e^{-i\phi_3} & 1 & e^{+i\phi_3} \end{vmatrix} \propto r_{12} r_{13} r_{23}$$

Mitas, PRL 96 (2006) 240402

Loos & Gill, PRL 108 (2012) 083002

Reduced correlation energy (in millihartree) for n electrons on a ring

n	η	Seitz radius r_s										
		0	0.1	0.2	0.5	1	2	5	10	20	50	100
2	3/4	13.212	12.985	12.766	12.152	11.250	9.802	7.111	4.938	3.122	1.533	0.848
3	8/9	18.484	18.107	17.747	16.755	15.346	13.179	9.369	6.427	4.030	1.965	1.083
4	15/16	21.174	20.698	20.249	19.027	17.324	14.762	10.390	7.085	4.425	2.150	1.184
5	24/25	22.756	22.213	21.66	20.33	18.439	15.644	10.946	7.439	4.636	2.248	1.237
6	35/36	23.775	23.184	22.63	21.14	19.137	16.192	11.285	7.653	4.762	2.307	1.268
7	48/49	24.476	23.850	23.24	21.70	19.607	16.554	11.509	7.795	4.844	2.345	1.289
8	63/64	24.981	24.328	23.69	22.11	19.940	16.808	11.664	7.890	4.901	2.370	1.302
9	80/81	25.360	24.686	24.04	22.39	20.186	16.995	11.777	7.960	4.941	2.389	1.312
10	99/100	25.651	24.960	24.25	22.62	20.373	17.134	11.857	8.013	4.973	2.404	1.320
∞	1	27.416	26.597	25.91	23.962	21.444	17.922	12.318	8.292	5.133	2.476	1.358

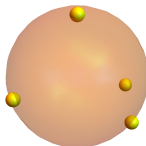
Loos & Gill, JCP 138 (2013) 164124; Loos, Ball & Gill, ibid 140 (2014) 18A524

Why on a Sphere?

Electrons on a sphere are cool!

- 1 One can hardly find something more **simple** and **symmetric**
- 2 ... and **symmetry** is your friend!
- 3 **Ferromagnetic** systems have **minimal number of nodal pockets**
Mitas, PRL 96 (2006) 240402
- 4 One can create **finite uniform electron gases**

Where are the nodes?



Spherical coordinates

$$x = \cos \phi \sin \theta$$

$$y = \sin \phi \sin \theta$$

$$z = \cos \theta$$

Orbitals on a sphere: $s, p, d, f, g, h, i, j, \dots$

$$\begin{array}{ccccccc}
 \overline{f_{y(3x^2-y^2)}} & \overline{f_{xyz}} & \overline{f_{yz^2}} & \overline{f_{z^3}} & \overline{f_{xz^2}} & \overline{f_{z(x^2-y^2)}} & \overline{f_{(x^2-3y^2)}} \\
 & \overline{d_{xy}} & \overline{d_{yz}} & \overline{d_{z^2}} & \overline{d_{xz}} & \overline{d_{x^2-y^2}} & \\
 & & \overline{p_y} & \overline{p_z} & \overline{p_x} & & \\
 & & & \overline{s} & & &
 \end{array}$$

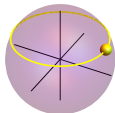
Loos & Gill, PRA 79 (2009) 062517; PRL 103 (2009) 123008; Mol. Phys. 108 (2010) 2527.

Two Electrons on a Sphere

sp state: ${}^3P^o$

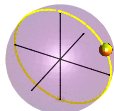
$$\Psi_0 = \begin{vmatrix} 1 & z_1 \\ 1 & z_2 \end{vmatrix}$$

$$= \mathbf{z} \cdot \mathbf{r}_{12}$$

p² state: ${}^3P^e$

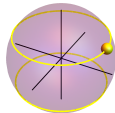
$$\Psi_0 = \begin{vmatrix} x_1 & y_1 \\ x_2 & y_2 \end{vmatrix}$$

$$= \mathbf{z} \cdot \mathbf{r}_{12}^{\times}$$

sd state: ${}^3D^e$

$$\Psi_0 = \begin{vmatrix} 1 & x_1 y_1 \\ 1 & x_2 y_2 \end{vmatrix}$$

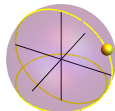
$$= (\mathbf{z} \cdot \mathbf{r}_{12}^+) (\mathbf{z} \cdot \mathbf{r}_{12})$$

pd state: ${}^3D^o$

$$\Psi_0 = \begin{vmatrix} y_1 & x_1 z_1 \\ y_2 & x_2 z_2 \end{vmatrix}$$

$$- \begin{vmatrix} x_1 & y_1 z_1 \\ x_2 & y_2 z_2 \end{vmatrix}$$

$$= (\mathbf{z} \cdot \mathbf{r}_{12}^+) (\mathbf{z} \cdot \mathbf{r}_{12}^{\times})$$



$\mathbf{z} = (0, 0, 1)$ is the unit vector of the z axis, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{r}_{ij}^+ = \mathbf{r}_i + \mathbf{r}_j$ and $\mathbf{r}_{ij}^{\times} = \mathbf{r}_i \times \mathbf{r}_j$

Loos & Gill, PRA 79 (2009) 062517; PRL 103 (2009) 123008; Mol. Phys. 108 (2010) 2527

Loos & Bressanini, JCP 142 (2015) 214112; Pechukas, JCP 57 (1972) 5577.

Exact solution for two-electron systems

Ground state and excited states of D -spherium

$$\Phi(\{\Omega_1, \Omega_2\}, r_{12}) = \Psi_0(\Omega_1, \Omega_2)\Lambda(r_{12})$$

State	Configuration	$\Psi_0(\Omega_1, \Omega_2)$	δ	γ^{-1}	D _{2h} IR	Interdim. degeneracy
$^1S^e$	s^2	1	$2D - 1$	$D - 1$	A _g	$^3P^e$
$^3P^o$	sp	$\mathbf{z} \cdot \mathbf{r}_{12}$	$2D + 1$	$D + 1$	B _{1u}	$^1D^o$
$^1P^o$	sp	$\mathbf{z} \cdot \mathbf{r}_{12}^+$	$2D + 1$	$D - 1$	B _{1u}	$^3D^o$
$^3P^e$	p^2	$\mathbf{z} \cdot \mathbf{r}_{12}^\times$	$2D + 3$	$D + 1$	B _{1g}	
$^3D^e$	sd	$(\mathbf{z} \cdot \mathbf{r}_{12})(\mathbf{z} \cdot \mathbf{r}_{12}^+)$	$2D + 3$	$D + 1$	A _g	$^1F^e$
$^1D^o$	pd	$(\mathbf{z} \cdot \mathbf{r}_{12})(\mathbf{z} \cdot \mathbf{r}_{12}^\times)$	$2D + 5$	$D + 3$	A _u	
$^3D^o$	pd	$(\mathbf{z} \cdot \mathbf{r}_{12}^+)(\mathbf{z} \cdot \mathbf{r}_{12}^\times)$	$2D + 5$	$D + 1$	A _u	
$^1F^e$	pf	$(\mathbf{z} \cdot \mathbf{r}_{12}^\times)(\mathbf{z} \cdot \mathbf{r}_{12})(\mathbf{z} \cdot \mathbf{r}_{12}^+)$	$2D + 7$	$D + 3$	B _{1g}	

$$\Lambda(r_{12}) = 1 + \gamma r_{12}$$

$$R = \sqrt{\frac{\delta}{4\gamma}}$$

$$E = \gamma$$

Interdimensional degeneracy: $1S^e \leftrightarrow 3P^e$ in He

$1S^e(1s^2)$ in D dimensions

$$-\frac{1}{2}\Delta^{(D)}\Lambda + \left(-\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right)\Lambda = E\Lambda$$

Λ is a nodeless, totally symmetric function of r_1 , r_2 and r_{12} for any value of $D \geq 2$

$3P^e(2p^2)$ in $D - 2$ dimensions

$$\Phi = \Psi_0 \Lambda \quad \text{with} \quad \Psi_0 = (x_1 y_2 - y_1 x_2)$$

$$\begin{aligned} \Delta^{(D-2)}\Phi &= \Psi_0 \left[\Delta^{(D-2)}\Lambda + \left(\frac{2}{r_1} \frac{\partial \Lambda}{\partial r_1} + \frac{2}{r_2} \frac{\partial \Lambda}{\partial r_2} + \frac{4}{r_{12}} \frac{\partial \Lambda}{\partial r_{12}} \right) \right] \\ &= \Psi_0 \Delta^{(D)}\Lambda \end{aligned}$$

$\Rightarrow \Lambda$ is a nodeless, totally symmetric function of r_1 , r_2 and r_{12} , and nodes are given by Ψ_0

NB: A similar relationship can be obtained between $3S^e(1s2s)$ in 5D and $1P^e(2p^2)$ in 3D
Herrick, J Math Phys 16 (1975) 281

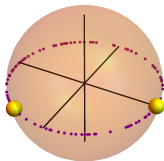
Are the HF nodes of the p^3 state exact?

p^3 state: $4S^0$

$$\begin{aligned}\Psi_0 &= \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \\ &= \mathbf{r}_1 \cdot (\mathbf{r}_2 \times \mathbf{r}_3)\end{aligned}$$

$|\Psi_0|$ = volume of **parallelepiped**

HF nodes vs FCI nodes



● HF

Proof: great circles are nodes!

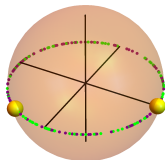
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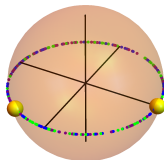
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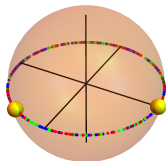
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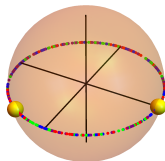
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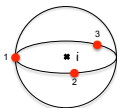
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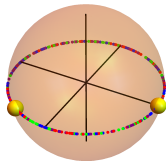
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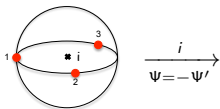
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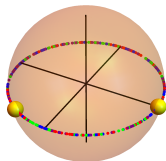
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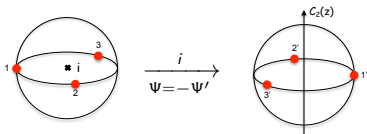
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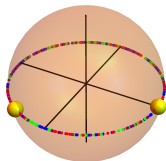
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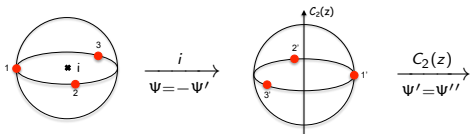
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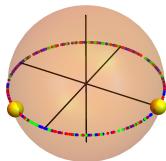
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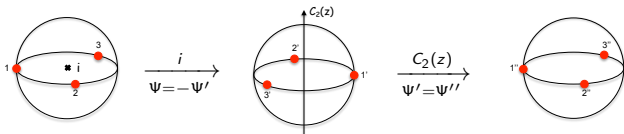
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Interdimensional degeneracy

Fermionic excited state \leftrightarrow bosonic ground state

Fermionic p^3 state in 3D is degenerate with bosonic s^3 state in 5D

$$\Delta^{(3)}\Phi = \Delta^{(3)}\Psi_0 \Lambda = \Psi_0 \Delta^{(5)}\Lambda$$

where

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix}$$

Φ and Ψ_0 are antisymmetric

$\Rightarrow \Lambda$ is a totally symmetric function

$\Rightarrow \Lambda$ is the ground-state wave function of the spinless bosonic s^3 state in 5D

$\Rightarrow \Lambda$ is nodeless and nodes are given by $\Psi_0!$

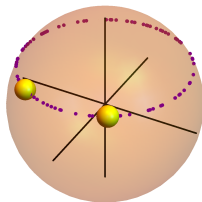
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Are the HF nodes of the sp^2 state exact?

sp^2 state: ${}^4D^e$

$$\begin{aligned}\psi_0 &= \begin{vmatrix} 1 & x_1 & y_1 \\ 1 & x_2 & y_2 \\ 1 & x_3 & y_3 \end{vmatrix} \\ &= \mathbf{z} \cdot (\mathbf{r}_{12} \times \mathbf{r}_{13})\end{aligned}$$

HF nodes vs FCI nodes



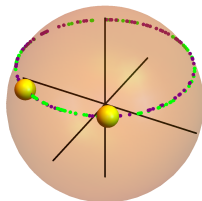
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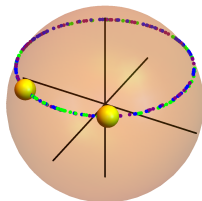
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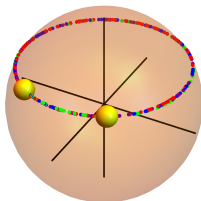
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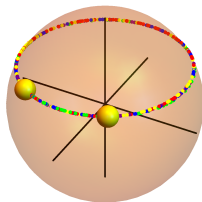
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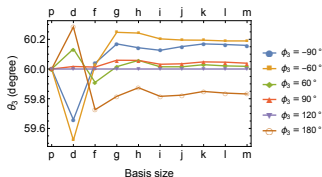
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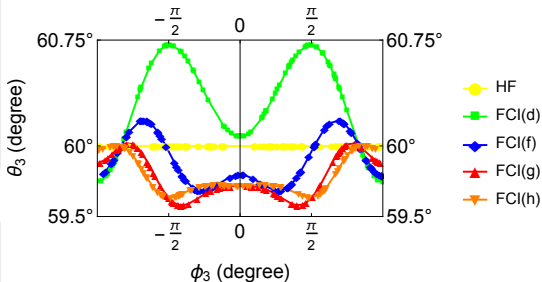
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'Experimental' non-proof



HF nodes vs FCI nodes



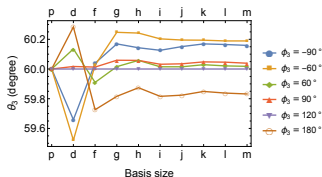
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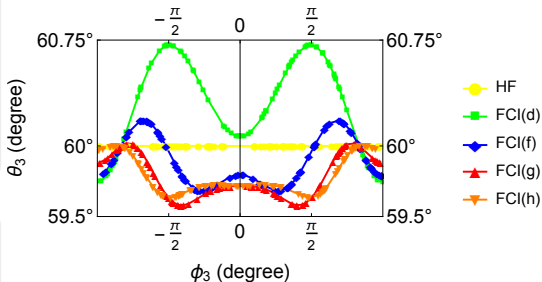
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HF nodes vs FCI nodes



The HF nodes of the sp^2 state are **not** exact!
 ... but not too bad!

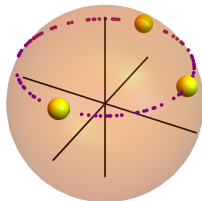
Are the HF nodes of the sp^3 state exact?

sp^3 state: ${}^5S^0$

$$\psi_0 = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix}$$

$$= (r_{12} + r_{34})(r_{12}^\times + r_{34}^\times)$$

HF nodes vs FCI nodes: small circles?



● HF

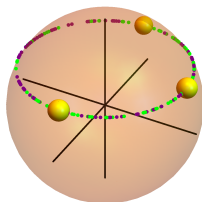
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HF nodes vs FCI nodes: small circles?



- HF
- FCI up to d functions

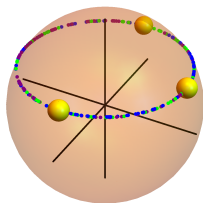
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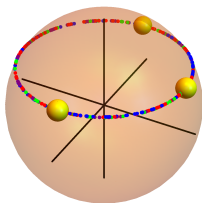
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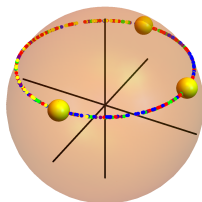
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- FCI up to g functions
- FCI up to h functions

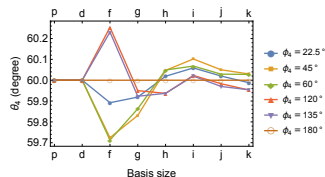
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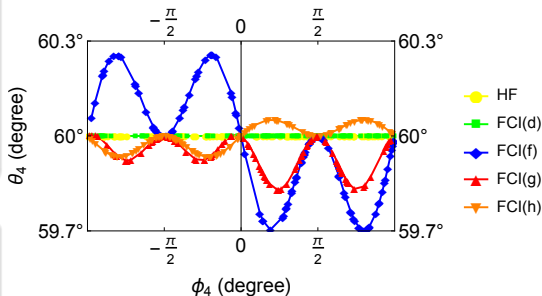
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Exact or not exact?



HF nodes vs FCI nodes: small circles?



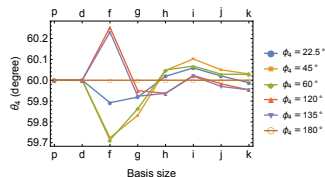
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HF nodes vs FCI nodes: small circles?

TABLE II. VMC and benchmark energies for various states at $r_s = 1$. The statistical errors are reported in parentheses.

States	VMC	Benchmark
${}^3P^o(sp)$	1.465 189 86(4)	1.465 189 850 ^a
${}^3P^e(p^2)$	2.556 684 32(9)	2.556 684 316 ^a
${}^3D^o(sd)$	3.556 684 32(9)	3.556 684 316 ^a
${}^3D^o(pd)$	4.635 924 8(2)	4.635 924 645 ^a
${}^4S^o(p^3)$	2.239 988 8(3)	2.239 988 9 ^a
${}^4D^e(sp^2)$	1.699 883(3)	1.699 872 ^b
${}^5S^o(sp^3)$	1.836 555 6(6)	1.836 556 ^b

^aHylleraas-type calculation.

^bExtrapolated FCI calculation.

The HF nodes of the sp^3 state **could be exact!**
 ... if not, they're really good!

A journey in four dimensions...

 p^4 state: 5S_e

$$\psi_0 = \begin{vmatrix} w_1 & x_1 & y_1 & z_1 \\ w_2 & x_2 & y_2 & z_2 \\ w_3 & x_3 & y_3 & z_3 \\ w_4 & x_4 & y_4 & z_4 \end{vmatrix}$$

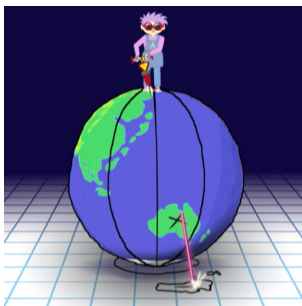
Hyperspherical coordinates

$$w = \cos \chi$$

$$x = \sin \chi \cos \phi \sin \theta$$

$$y = \sin \chi \sin \phi \sin \theta$$

$$z = \sin \chi \cos \theta$$

Stereographic projection of a 2- and 3-sphereConnection $p^4 \rightarrow sp^3$

sp^3 nodes are subset of p^4 and p^4 nodes are exact

Does it mean that the sp^3 nodes are exact?

Summary

To summarize what we discovered...

n	State	Configuration	$\Psi_0(\{\{\Omega_i\}\})$	Exact?
2	${}^3P^o$	sp	$\mathbf{z} \cdot \mathbf{r}_{12}$	Yes
2	${}^3P^e$	p^2	$\mathbf{z} \cdot \mathbf{r}_{12}^\times$	Yes
2	${}^3D^e$	sd	$(\mathbf{z} \cdot \mathbf{r}_{12}^+)(\mathbf{z} \cdot \mathbf{r}_{12})$	Yes
2	${}^3D^o$	pd	$(\mathbf{z} \cdot \mathbf{r}_{12}^+)(\mathbf{z} \cdot \mathbf{r}_{12}^\times)$	Yes
3	${}^4S^o$	p^3	$\mathbf{r}_1 \cdot \mathbf{r}_{23}^\times$	Yes
3	${}^4D^e$	sp^2	$\mathbf{z} \cdot (\mathbf{r}_{12} \times \mathbf{r}_{13})$	No
4	${}^5S^o$	sp^3	$(\mathbf{r}_{12} + \mathbf{r}_{34})(\mathbf{r}_{12}^\times + \mathbf{r}_{34}^\times)$	Unknown

Loos & Bressanini, JCP 142 (2015) 214112

More work is being done on the ground-state of the Li atom at the moment...

Concluding remarks

For same-spin electrons on a sphere,

- HF nodes are amazingly **accurate** (**sometimes exact**)
- **FCI** doesn't **always** improve the nodes
- **FN-DMC** should yield very accurate energies
- It can be used to get **near-exact** energies of **uniform electron gases**
... and create **new** density functionals
- It can be generalized to **more electrons** and **higher dimensions**
- It can probably be generalized to **Jerzium...**
- Is there a new family of **solvable nodal systems**? **Hidden algebra?**

Collaborators and Funding

- Collaborators:



Peter Gill



Dario Bressanini

- Research School of Chemistry & Australian National University
- Australian Research Council:
Discovery Early Career Researcher Award 2013 & Discovery Project 2014

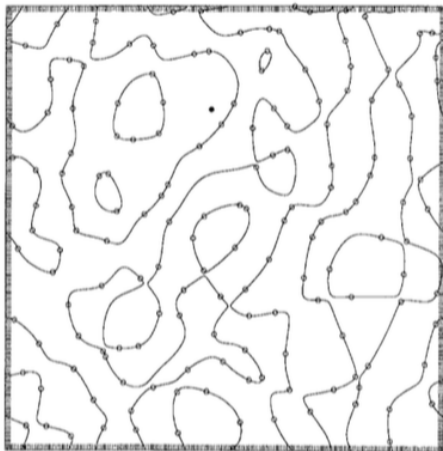


Australian Government
Australian Research Council

The Tiling Theorem

The tiling theorem

In the fermionic ground state, **all nodal pockets are equivalent**, i.e. they have the same shape, and the various permutations transform one pocket into another.



Ceperley, J Phys Stat 63 (1991) 1237

Note that this theorem does not specify the total number of nodal pockets

Always starts with He...

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The 1S ground state is trivial

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For the 3S state,

Always starts with He...

The 1S ground state is trivial

For the 3S state,

$$\Psi = \Psi(r_1, r_2, r_{12})$$

$$1 \leftrightarrow 2 \Rightarrow \Psi(r_1, r_2, r_{12}) = -\Psi(r_2, r_1, r_{12})$$

$$r_1 = r_2 = r \Rightarrow \Psi(r, r, r_{12}) = -\Psi(r, r, r_{12}) \Rightarrow \Psi(r, r, r_{12}) = 0$$

The nodes are given by $r_1 - r_2 = 0$ (more symmetric than Ψ ?)

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Note that $\Psi_{\text{HF}} = \begin{vmatrix} \varphi_{1s}(r_1) & \varphi_{1s}(r_2) \\ \varphi_{2s}(r_1) & \varphi_{2s}(r_2) \end{vmatrix}$ has exact nodes

Klein and Pickett 64 (1976) 4811

Nodes in the Be atom

Bressanini, PRB 86 (2012) 115120

Nodes in the Be atom

HF wave function for Be

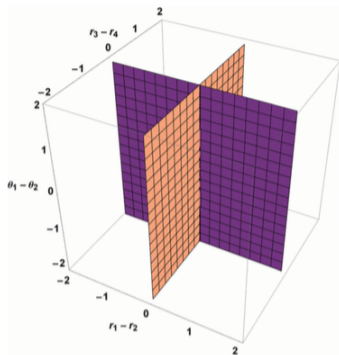


FIG. 1. (Color online) Three-dimensional cut of the full 11D node of the HF wave function for the Be atom with four nodal domains.

Bressanini, PRB 86 (2012) 115120

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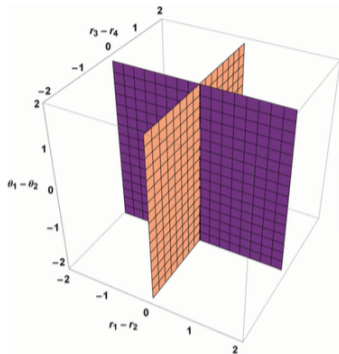


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CI wave function for Be

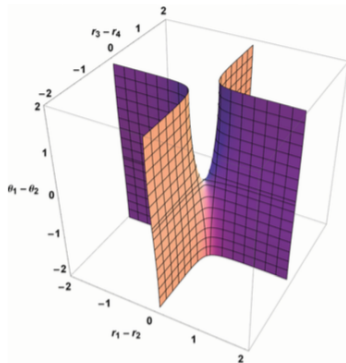


FIG. 2. (Color online) Three-dimensional cut of the full 11D node of the CI wave function for the Be atom with two nodal domains.

Bressanini, PRB 86 (2012) 115120

Proof for the Be atom

- There's at most 4 pockets (I , P_{12} , P_{34} and $P_{12} P_{34}$)

Bressanini, Ceperley and Reynolds, Recent Advances in Quantum Monte Carlo Methods, II, ed. S. Rothstein, World Scientific (2001).

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$$R^* = P_{12} P_{34} R^*$$

where Ψ does not change sign

Bressanini, Ceperley and Reynolds, Recent Advances in Quantum Monte Carlo Methods, II, ed. S. Rothstein, World Scientific (2001).

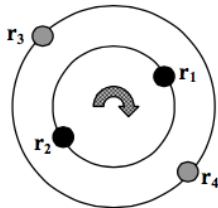
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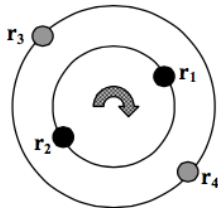
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- Let's try $R = (r_1, -r_1, r_3, -r_3)$ and rotate by π around $r_1 \times r_3$
- **Bingo!**



Bressanini, Ceperley and Reynolds, Recent Advances in Quantum Monte Carlo Methods, II, ed. S. Rothstein, World Scientific (2001).

What do you think?

The conjecture

In recent years, a body of evidence has accumulated showing that in several cases **the ground fermionic state has only two nodal domains**, the minimum possible, and it has been conjectured that this property might be a general property of fermionic systems.

Do you think it's true?