Nodal Surfaces in Quasi-Exactly Solvable Models

Pierre-François Loos,\textsuperscript{1} Peter Gill,\textsuperscript{1} and Dario Bressanini\textsuperscript{2}

\textsuperscript{1}Research School of Chemistry, Australian National University, Canberra, Australia

\textsuperscript{2}Dipartimento di Scienza e Alta Tecnologia, Università dell’Insubria, Como, Italy

16th Conference in Computational and Mathematical Methods in Science and Engineering, Cadiz, Spain

6th Jul 2016
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

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \eta )</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
</table>

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

\[
\begin{align*}
x &= \cos \phi \sin \theta \\
y &= \sin \phi \sin \theta \\
z &= \cos \theta
\end{align*}
\]

Orbitals on a sphere: \( s, p, d, f, g, h, i, j, \ldots \)

\[
\begin{align*}
f_y(3x^2-y^2) & \quad f_{xyz} \\
d_{xy} & \\
f_{yz} & \\
d_{yz} & \\
f_{z^2} & \\
d_{xz} & \\
f_{x^2-z^2} & \\
d_{x^2-y^2} & \\
f_{yz} & \\
d_{yz} & \\
f_{z^3} & \\
d_{z^2} & \\
f_{x^2-z^2} & \\
d_{x^2-y^2} & \\
f_{y}(3x^2-y^2) & \\
d_{xy} & \\
f_{z^3} & \\
d_{z^2} & \\
f_{x^2-z^2} & \\
d_{x^2-y^2} & \\
f_{yz} & \\
d_{yz} & \\
f_{z^3} & \\
d_{z^2} & \\
f_{x^2-z^2} & \\
d_{x^2-y^2} & \\
f_{y}(3x^2-y^2) & \\
d_{xy} & \\
f_{z^3} & \\
d_{z^2} & \\
f_{x^2-z^2} & \\
d_{x^2-y^2} & \\
f_{y}(3x^2-y^2) &
\end{align*}
\]
Two Electrons on a Sphere

**sp state:** $^3P^o$

\[
\psi_0 = \begin{bmatrix} 1 & z_1 \\ 1 & z_2 \end{bmatrix}
\]

\[= z \cdot r_{12} \]

**$p^2$ state:** $^3P^e$

\[
\psi_0 = \begin{bmatrix} x_1 & y_1 \\ x_2 & y_2 \end{bmatrix}
\]

\[= z \cdot r_{12}^x \]

**sd state:** $^3D^e$

\[
\psi_0 = \begin{bmatrix} 1 & x_1 y_1 \\ 1 & x_2 y_2 \end{bmatrix}
\]

\[= (z \cdot r_{12}^+) (z \cdot r_{12}) \]

**pd state:** $^3D^o$

\[
\psi_0 = \begin{bmatrix} y_1 & x_1 z_1 \\ y_2 & x_2 z_2 \end{bmatrix}
\]

\[= (z \cdot r_{12}^+) (z \cdot r_{12}^x) \]

$z = (0, 0, 1)$ is the unit vector of the $z$ axis, $r_{ij} = r_i - r_j$, $r_{ij}^+ = r_i + r_j$ and $r_{ij}^x = r_i \times r_j$

Loos & Bressanini, JCP 142 (2015) 214112; Pechukas, JCP 57 (1972) 5577.
**Ground state and excited states of $D$-spherium**

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

<table>
<thead>
<tr>
<th>State</th>
<th>Configuration</th>
<th>$\Psi_0(\Omega_1, \Omega_2)$</th>
<th>$\delta$</th>
<th>$\gamma^{-1}$</th>
<th>$D_{2h}$ IR</th>
<th>Interdim. degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S^e$</td>
<td>$s^2$</td>
<td>1</td>
<td>$2D - 1$</td>
<td>$D - 1$</td>
<td>$A_g$</td>
<td>$^3P^e$</td>
</tr>
<tr>
<td>$^3P^o$</td>
<td>$sp$</td>
<td>$z \cdot r_{12}$</td>
<td>$2D + 1$</td>
<td>$D + 1$</td>
<td>$B_{1u}$</td>
<td>$^1D^o$</td>
</tr>
<tr>
<td>$^1P^o$</td>
<td>$sp$</td>
<td>$z \cdot r_{12}^+$</td>
<td>$2D + 1$</td>
<td>$D - 1$</td>
<td>$B_{1u}$</td>
<td>$^3D^o$</td>
</tr>
<tr>
<td>$^3P^e$</td>
<td>$p^2$</td>
<td>$z \cdot r_{12}^x$</td>
<td>$2D + 3$</td>
<td>$D + 1$</td>
<td>$B_{1g}$</td>
<td>$^1F^e$</td>
</tr>
<tr>
<td>$^3D^e$</td>
<td>$sd$</td>
<td>$(z \cdot r_{12})(z \cdot r_{12}^x)$</td>
<td>$2D + 3$</td>
<td>$D + 1$</td>
<td>$A_g$</td>
<td>$^1F^e$</td>
</tr>
<tr>
<td>$^1D^o$</td>
<td>$pd$</td>
<td>$(z \cdot r_{12})(z \cdot r_{12}^x)$</td>
<td>$2D + 5$</td>
<td>$D + 3$</td>
<td>$A_u$</td>
<td>$^1F^e$</td>
</tr>
<tr>
<td>$^3D^o$</td>
<td>$pd$</td>
<td>$(z \cdot r_{12}^+)(z \cdot r_{12}^x)$</td>
<td>$2D + 5$</td>
<td>$D + 1$</td>
<td>$A_u$</td>
<td>$^1F^e$</td>
</tr>
<tr>
<td>$^1F^e$</td>
<td>$pf$</td>
<td>$(z \cdot r_{12}^x)(z \cdot r_{12})(z \cdot r_{12}^+)$</td>
<td>$2D + 7$</td>
<td>$D + 3$</td>
<td>$B_{1g}$</td>
<td>$^1F^e$</td>
</tr>
</tbody>
</table>

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

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

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

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

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

$\Lambda$ 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

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

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

$$= \Psi_0 \Delta^{(D)} \Lambda$$

$\Rightarrow \Lambda$ is a nodeless, totally symmetric function of $r_1$, $r_2$ and $r_{12}$, and nodes are given by $\Psi_0$

**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: $^4S^o$

\[ \Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3) \]

\[ |\Psi_0| = \text{volume of parallelepiped} \]

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$|\Psi_0| = \text{volume of parallelepiped}$

**Proof**: great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$|\Psi_0| =$ volume of parallelepiped

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

**$p^3$ state:** $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$|\Psi_0| = \text{volume of parallelepiped}$

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^0$

\[ \Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3) \]

\[ |\Psi_0| = \text{volume of parallelepiped} \]

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$|\Psi_0| = \text{volume of parallelepiped}$

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$|\Psi_0| =$ volume of parallelepiped

**Proof:** great circles are nodes!
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$$

$$|\Psi_0| = \text{volume of parallelepiped}$$

Proof: great circles are nodes!

**HF nodes vs FCI nodes**

- HF
- FCI up to $d$ functions
- FCI up to $f$ functions
- FCI up to $g$ functions
Are the HF nodes of the $p^3$ state exact?

$p^3$ state: $^4S^o$

$\Psi_0 = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} = r_1 \cdot (r_2 \times r_3)$

$|\Psi_0| = \text{volume of parallelepiped}$

Proof: great circles are nodes!
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

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

$\Phi$ and $\Psi_0$ 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 $\Psi_0$!

Herrick, J Math Phys 16 (1975) 281
Are the HF nodes of the $sp^2$ state exact?

$s^2$ state: $^4D^e$

$$\Psi_0 = \begin{vmatrix} 1 & x_1 & y_1 \\ 1 & x_2 & y_2 \\ 1 & x_3 & y_3 \end{vmatrix} = z \cdot (r_{12} \times r_{13})$$

**HF nodes vs FCI nodes**
Are the HF nodes of the $sp^2$ state exact?

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

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

$$= z \cdot (r_{12} \times r_{13})$$

HF nodes vs FCI nodes
Are the HF nodes of the \( sp^2 \) state exact?

\( sp^2 \) state: \( ^4D^e \)

\[
\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 \\
1 & x_2 & y_2 \\
1 & x_3 & y_3 \\
\end{vmatrix}
\]

\[= z \cdot (r_{12} \times r_{13})\]

HF nodes vs FCI nodes

- \( \bullet \) HF
- \( \bullet \) FCI up to \( d \) functions
- \( \bullet \) FCI up to \( f \) functions
Are the HF nodes of the $sp^2$ state exact?

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

$$
\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 \\
1 & x_2 & y_2 \\
1 & x_3 & y_3 \\
\end{vmatrix}
= z \cdot (r_{12} \times r_{13})
$$
Are the HF nodes of the \( sp^2 \) state exact?

\[ sp^2 \text{ state: } 4D^e \]

\[
\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 \\
1 & x_2 & y_2 \\
1 & x_3 & y_3 \\
\end{vmatrix}
= z \cdot (r_{12} \times r_{13})
\]

**HF nodes vs FCI nodes**

- HF
- FCI up to \( d \) functions
- FCI up to \( f \) functions
- FCI up to \( g \) functions
- FCI up to \( h \) functions
Are the HF nodes of the $sp^2$ state exact?

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

$$
\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 \\
1 & x_2 & y_2 \\
1 & x_3 & y_3 \\
\end{vmatrix}
= z \cdot (r_{12} \times r_{13})
$$

'Experimental' non-proof

HF nodes vs FCI nodes

Pierre-François Loos (RSC, ANU)
Nodal surfaces in quasi-exactly solvable models
CMMSE16 — 6th Jul 2016 — 10 / 20
Are the HF nodes of the $sp^2$ state exact?

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

$$\Psi_0 = \begin{vmatrix} 1 & x_1 & y_1 \\ 1 & x_2 & y_2 \\ 1 & x_3 & y_3 \end{vmatrix} = z \cdot (r_{12} \times r_{13})$$

‘Experimental’ non-proof

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: $^5S^o$

$$\Psi_0 = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix} = (r_{12} + r_{34})(r_{12}^x + r_{34}^x)$$

HF nodes vs FCI nodes: small circles?
Are the HF nodes of the $sp^3$ state exact?

$sp^3$ state: $^5S^o$

$$\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 & z_1 \\
1 & x_2 & y_2 & z_2 \\
1 & x_3 & y_3 & z_3 \\
1 & x_4 & y_4 & z_4 \\
\end{vmatrix} = (r_{12} + r_{34})(r_{12}^x + r_{34}^x)$$

HF nodes vs FCI nodes: small circles?
Are the HF nodes of the $sp^3$ state exact?

$sp^3$ state: $^5S^o$

$$\Psi_0 = \begin{vmatrix}
1 & x_1 & y_1 & z_1 \\
1 & x_2 & y_2 & z_2 \\
1 & x_3 & y_3 & z_3 \\
1 & x_4 & y_4 & z_4
\end{vmatrix} = (r_{12} + r_{34})(r_{12}^{\times} + r_{34}^{\times})$$

HF nodes vs FCI nodes: small circles?

- HF
- FCI up to $d$ functions
- FCI up to $f$ functions
Are the HF nodes of the $sp^3$ state exact?

$sp^3$ state: $^5S^o$

$$\psi_0 = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix} = (r_{12} + r_{34})(r_{12}^x + r_{34}^x)$$

HF nodes vs FCI nodes: small circles?
Are the HF nodes of the $sp^3$ state exact?

$sp^3$ state: $^5S^o$

$$\Psi_0 = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix} = (r_{12} + r_{34})(r_{12}^\times + r_{34}^\times)$$

HF nodes vs FCI nodes: small circles?

- HF
- FCI up to $d$ functions
- FCI up to $f$ functions
- FCI up to $g$ functions
- FCI up to $h$ functions
Are the HF nodes of the $sp^3$ state exact?

$sp^3$ state: $^5S^o$

$$\Psi_0 = \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix} = (r_{12} + r_{34})(r_{12}^\times + r_{34}^\times)$$

Exact or not exact?
Are the HF nodes of the \(sp^3\) state exact?

\[sp^3\text{ state: } ^5S^0\]

\[
\psi_0 = \begin{vmatrix}
1 & x_1 & y_1 & z_1 \\
1 & x_2 & y_2 & z_2 \\
1 & x_3 & y_3 & z_3 \\
1 & x_4 & y_4 & z_4
\end{vmatrix} = (r_{12} + r_{34})(r_{12}^x + r_{34}^x)
\]

**HF nodes vs FCI nodes: small circles?**

<table>
<thead>
<tr>
<th>States</th>
<th>VMC</th>
<th>Benchmark</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3P^0(sp))</td>
<td>1.465 189 86(4)</td>
<td>1.465 189 850(^a)</td>
</tr>
<tr>
<td>(^3P^e(p^2))</td>
<td>2.556 684 32(9)</td>
<td>2.556 684 316(^a)</td>
</tr>
<tr>
<td>(^3D^e(sd))</td>
<td>3.556 684 32(9)</td>
<td>3.556 684 316(^a)</td>
</tr>
<tr>
<td>(^3D^0(pd))</td>
<td>4.635 924 8(2)</td>
<td>4.635 924 645(^a)</td>
</tr>
<tr>
<td>(^4S^0(p^3))</td>
<td>2.239 988 8(3)</td>
<td>2.239 988 9(^a)</td>
</tr>
<tr>
<td>(^4P^e(sp^2))</td>
<td>1.699 883(3)</td>
<td>1.699 872(^b)</td>
</tr>
<tr>
<td>(^5S^0(sp^3))</td>
<td>1.836 555 6(6)</td>
<td>1.836 556(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Hylleraas-type calculation.  
\(^b\)Extrapolated FCI calculation.

The HF nodes of the \(sp^3\) state **could be** exact!  
... if not, they’re **really good**!
A journey in four dimensions...

**p⁴ 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**

\[
\begin{align*}
  w &= \cos \chi \\
  x &= \sin \chi \cos \phi \sin \theta \\
  y &= \sin \chi \sin \phi \sin \theta \\
  z &= \sin \chi \cos \theta
\end{align*}
\]

**Stereographic projection of a 2- and 3-sphere**

**Connection** \(p^4 \rightarrow sp^3\)

\(sp^3\) 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...

<table>
<thead>
<tr>
<th>$n$</th>
<th>State</th>
<th>Configuration</th>
<th>$\Psi_0({\Omega_i})$</th>
<th>Exact?</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$^3P^o$</td>
<td>$sp$</td>
<td>$z \cdot r_{12}$</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>$^3P^e$</td>
<td>$p^2$</td>
<td>$z \cdot r_{12}^x$</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>$^3D^e$</td>
<td>$sd$</td>
<td>$(z \cdot r_{12}^+)(z \cdot r_{12})$</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>$^3D^o$</td>
<td>$pd$</td>
<td>$(z \cdot r_{12}^+)(z \cdot r_{12}^x)$</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>$^4S^o$</td>
<td>$p^3$</td>
<td>$r_{1} \cdot r_{23}^x$</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>$^4D^e$</td>
<td>$sp^2$</td>
<td>$z \cdot (r_{12} \times r_{13})$</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>$^5S^o$</td>
<td>$sp^3$</td>
<td>$(r_{12} + r_{34})(r_{12}^x + r_{34}^x)$</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

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
Fermionic nodes

The Tilling Theorem

The tilling 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...
Always starts with He...

The $^1S$ ground state is trivial
Always starts with He...

The $^1S$ ground state is trivial

For the $^3S$ state,
Always starts with He...

The $^1S$ ground state is trivial

For the $^3S$ state,

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

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

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

The nodes are given by $r_1 - r_2 = 0$ (more symmetric than $\Psi$?)
Always starts with He...

The $^1S$ ground state is trivial

For the $^3S$ state,

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

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

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

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

**NB:** It does include Pauli nodes $r_1 - r_2 = 0$ (*dimension?*)
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 $\Psi$?)

NB: It does include Pauli nodes $r_1 - r_2 = 0$ (dimension?)

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

Bressanini, PRB 86 (2012) 115120
Nodes in the Be atom

**HF wave function for Be**

*Bressanini, PRB 86 (2012) 115120*

**CI wave function for Be**

*Bressanini, PRB 86 (2012) 115120*
Proof for the Be atom

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

Proof for the Be atom

- There’s at most 4 pockets ($I$, $P_{12}$, $P_{34}$ and $P_{12} P_{34}$)
- They look all the same (tiling theorem)

Proof for the Be atom

- There’s at most 4 pockets \((I, P_{12}, P_{34} \text{ and } P_{12} P_{34})\)
- They look all the same (tiling theorem)
- Starting from \(R^*\) with \(\Psi(R^*) \neq 0\), we must find a path such as:

\[
R^* = P_{12} P_{34} R^*
\]

where \(\Psi\) does not change sign

Proof for the Be atom

- There’s at most 4 pockets ($I, P_{12}, P_{34}$ and $P_{12} P_{34}$)
- They look all the same (tilling theorem)
- Starting from $\mathbf{R}^*$ with $\Psi(\mathbf{R}^*) \neq 0$, we must find a path such as:

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

where $\Psi$ does not change sign
- Let’s try $\mathbf{R} = (r_1, -r_1, r_3, -r_3)$ and rotate by $\pi$ around $r_1 \times r_3$

**Proof for the Be atom**

- There’s at most 4 pockets \((I, P_{12}, P_{34} \text{ and } P_{12} P_{34})\)
- They look all the same (tilling theorem)
- Starting from \(R^*\) with \(\Psi(R^*) \neq 0\), we must find a path such as:
  \[
  R^* = P_{12} P_{34} R^*
  \]
  where \(\Psi\) does not change sign
- Let’s try \(R = (r_1, -r_1, r_3, -r_3)\) and rotate by \(\pi\) around \(r_1 \times r_3\)
- Bingo!

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?