variational Richardson-Gaudin

Stijn De Baerdemacker[1,2]
for the Gemini[1,2,3,4]

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CECAM Valence Bond
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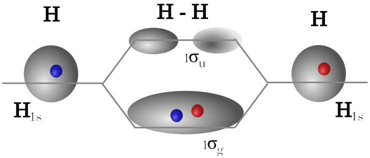
H_2, the fundamental geminal



- For *every* $2e^-$ problem

$$|H_2\rangle = \sum_{ij=1}^{2L} c_{ij} a_i^\dagger a_j^\dagger |\theta\rangle = \sum_{k=1}^{L} \lambda_k \tilde{a}_k^\dagger \tilde{a}_{\bar{k}}^\dagger |\theta\rangle$$

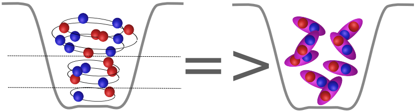
- $\tilde{a}_k^\dagger \tilde{a}_{\bar{k}}^\dagger = S_k^\dagger$ creates a pair

$\rightarrow$ $\tilde{a}_{\bar{k}} \tilde{a}_k = S_k$ annihilates this pair

Geminals

geminal states

$$|\mathrm{APG}\rangle = \prod_{\alpha=1}^{N}\sum_{i=1}^{L} G_{\alpha i} S_i^\dagger |\theta\rangle$$



- mean field state for pairs
- G is the Geminal matrix

1953 Proposed by Hurley, Lennard-Jones & Pople ✎

1959 Coined by Shull ✍

→ natural Geminals eigenvectors of 2DM

1969 APIG proposed by Silver ✐

✎ Proc. Roy. Soc. A220, 446 (1953)
✍ J. Chem. Phys. 30, 1405 (1959)
✐ J. Chem. Phys. 50, 5108 (1969)

Geminals: matrix elements

- Geminal states

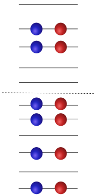
$$|\mathrm{APG}\rangle = \prod_{\alpha=1}^{N} \sum_{i=1}^{L} G_{\alpha i} S_i^\dagger |\theta\rangle$$

- Slater Determinants

$$|\mathrm{SD}\rangle = \prod_{\alpha=1}^{N} S_{i_\alpha}^\dagger |\theta\rangle$$

Overlap

$$\langle \mathrm{SD}|\mathrm{APG}\rangle = \mathrm{per}(\tilde{G})$$



$$\tilde{G} = \begin{pmatrix} G_{1i_1} & G_{1i_2} & \dots & G_{1i_N} \\ G_{2i_1} & G_{2i_2} & \dots & G_{2i_N} \\ \vdots & \vdots & \ddots & \vdots \\ G_{Ni_1} & G_{Ni_2} & \dots & G_{Ni_N} \end{pmatrix}$$

- The permanent is the symmetric brother of the determinant

$$\det(G) = \sum_{\sigma \in S_N} (-)^\sigma G_{1\sigma(1)} G_{2\sigma(2)} \dots G_{N\sigma(N)}$$

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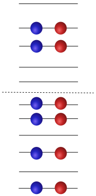

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Richardson's solution for the pairing problem

- The reduced BCS model is exactly solvable

$$H = \sum_{i=1}^{L} \varepsilon_i n_i + g \sum_{ij=1}^{L} S_i^\dagger S_j$$

- by means of a Bethe Ansatz product wavefunction

$$|\psi\rangle = \prod_{\alpha=1}^{N} S_\alpha^\dagger |\theta\rangle \qquad \text{with} \qquad S_\alpha^\dagger = \sum_{i=1}^{L} \frac{S_i^\dagger}{2\varepsilon_i - x_\alpha}$$

- provided the parameters x_α fullfill the

Richardson-Gaudin (RG) equations

$$1 + 2g \sum_{i=1}^{L} \frac{d_i}{2\varepsilon_i - x_\alpha} - 2g \sum_{\beta \neq \alpha}^{N} \frac{1}{x_\beta - x_\alpha} = 0 \qquad (\forall \alpha = 1 \ldots N)$$

Correlation functions

Geminal states

- generalized richardson states

$$|\mathrm{APG}\rangle = \prod_{\alpha=1}^{N}\sum_{i=1}^{L} G_{\alpha i} S_i^{\dagger}|\theta\rangle$$

- overlap with slater states

$$\langle \mathrm{Slater}|\mathrm{APG}\rangle = \mathrm{Per}(G)$$

- factorial scaling

Richardson states

- special geminal states

$$|\mathrm{RG}\rangle = \prod_{\alpha=1}^{N}\sum_{i=1}^{L} \frac{S_i^{\dagger}}{2\varepsilon_i - x_\alpha}|\theta\rangle$$

- overlap with slater states ✍

$$\langle \mathrm{Slater}|\mathrm{RG}\rangle = \frac{\det(RG*RG)}{\det(RG)}$$

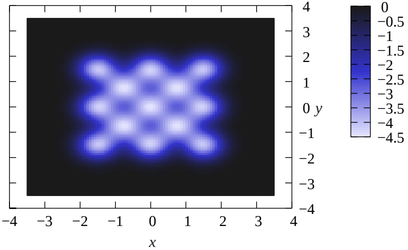
✍ Borchardt, Crelle J. 53, 193 (1855)

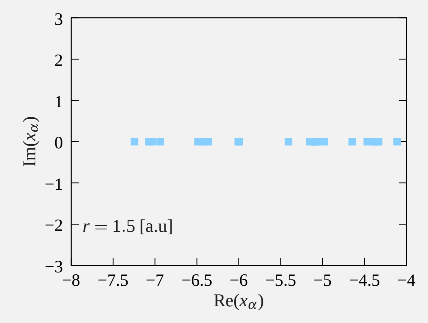
Can it work for static correlations?

- Richardson product state

$$|\psi\rangle = \prod_{\alpha=1}^{N} \sum_{i=1}^{L} \frac{S_i^\dagger}{2\varepsilon_i - x_\alpha} |\theta\rangle$$

- optical lattice
  $L \sim 80$ sp levels
  $N = 26$ pairs





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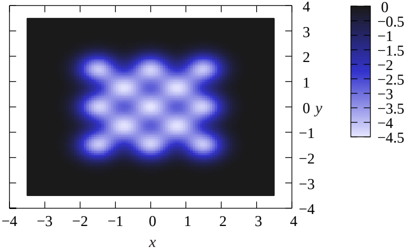

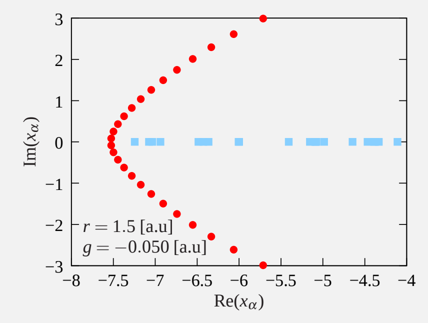

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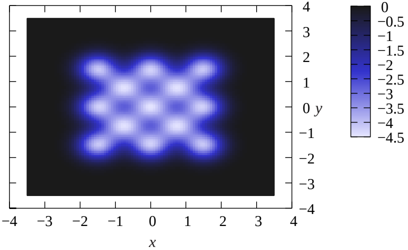

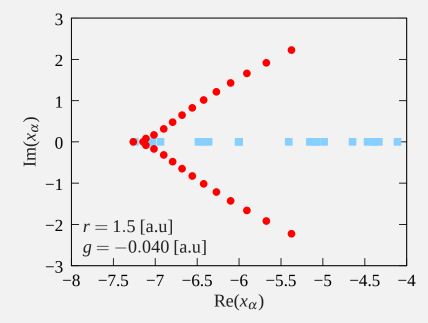

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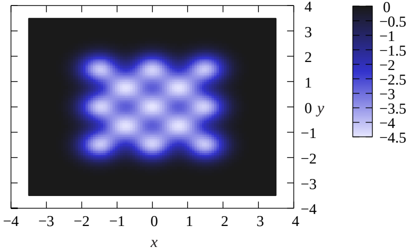

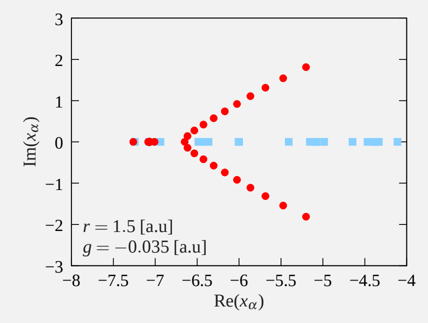

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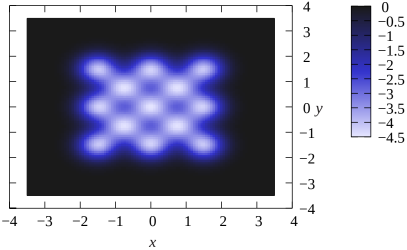

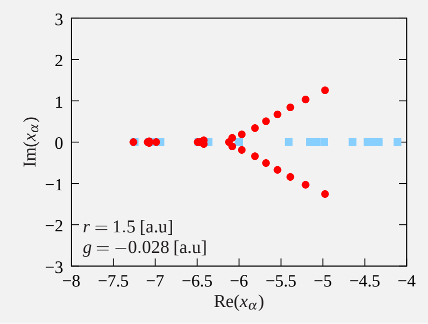

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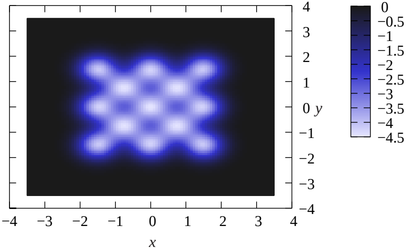

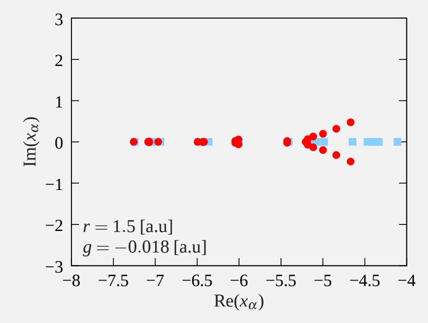

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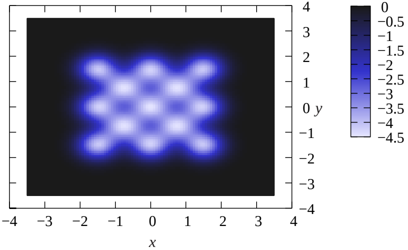

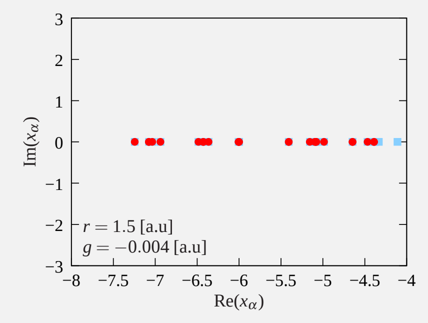

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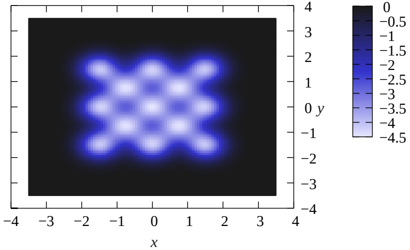

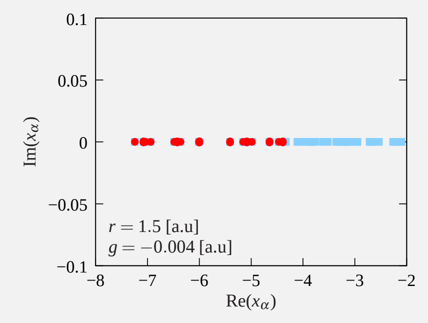

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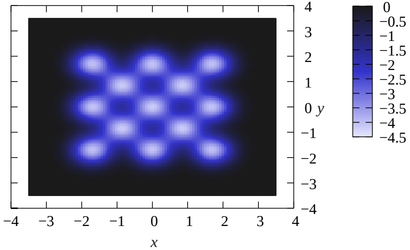

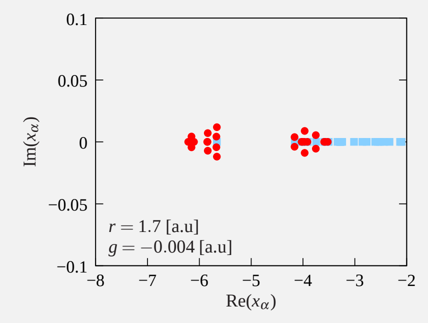

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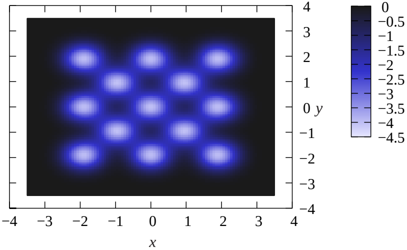

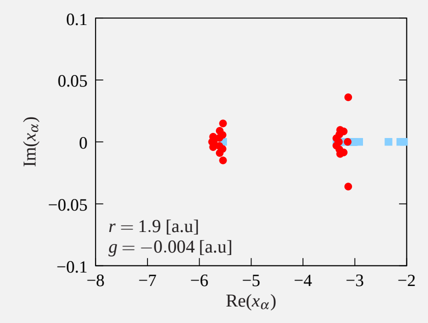

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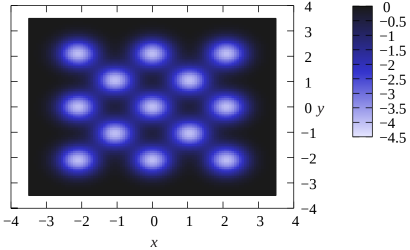

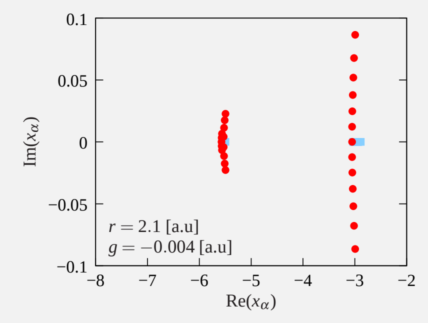

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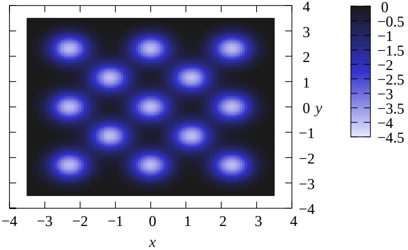

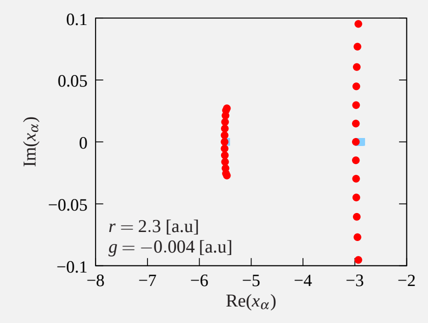

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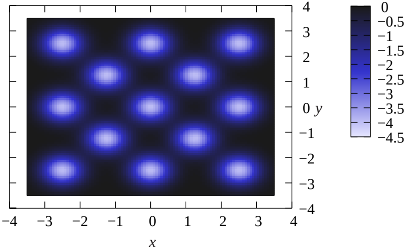
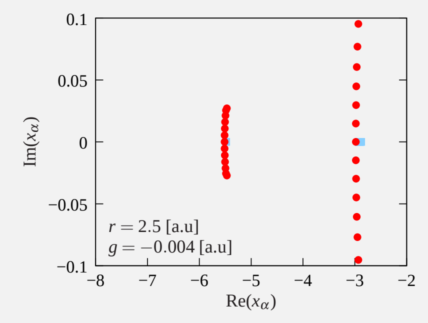




variational RG

- Access to tractable 2DM
- RG as Variational ansatz

$$E[\varepsilon_i] = \langle \mathrm{RG}(\varepsilon_i)|H|\mathrm{RG}(\varepsilon_i)\rangle$$

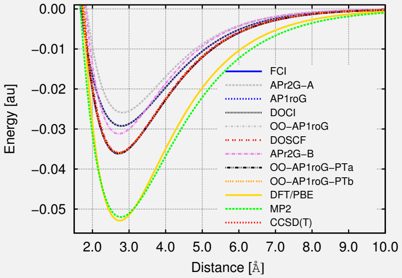
- $\min_{\varepsilon_i} E[\varepsilon_i]$ on manifold of integrable models

$$1+\sum_{i=1}^{L}\frac{2gd_i}{2\varepsilon_i - x_\alpha} - \sum_{\beta\neq\alpha}^{N}\frac{2g}{x_\beta - x_\alpha} = 0$$

- Discrete/continuous optimization problem

Li_2 in cc-pVDZ ✍

- APr2G-A: MO orbitals
- APr2G-B: OO-AP1roG orbitals



✍ P. Tecmer, et. al. (2014) J. Phys. Chem. A118, 9058

AP1roG

- AP$n$roG picks n occupied orbitals and leaves virtuals free

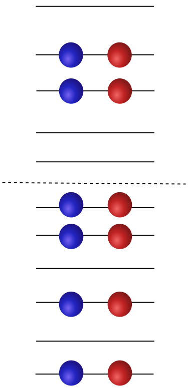
$$|\text{AP1roG}\rangle = \prod_{\alpha=1}^{N}\left(S_\alpha^\dagger + \sum_{i=N+1}^{L} c_\alpha^i S_i^\dagger\right)|\theta\rangle$$

- Geminal matrix

$$G_{\text{AP1roG}} = (\mathbf{1}_{N\times N}|\mathbf{c})$$

- projected Schrödinger approach: reference states

$$\langle\psi_{\text{ref}}|H|\text{AP1rog}\rangle = E\langle\psi_{\text{ref}}|\text{AP1rog}\rangle$$



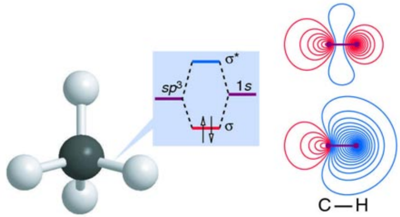
✎ P. A. Limacher, P. W. Ayers, P. A. Johnson, sdb, D. Van Neck, P. Bultinck; JCTC 9, 1394 (2013)

AP1roG for CH_4

- AP1roG in pSE (STO-6G)

$$\prod_{\alpha=1}^{N=5}\left(S_\alpha^\dagger + \sum_{i=6}^{9} G_{\alpha i} S_i^\dagger\right)|\theta\rangle$$

- OO = hybridisation (Lewis)



$$G = \left(\begin{array}{ccccc|cccc} 1 & 0 & 0 & 0 & 0 & -.001 & -.001 & -.001 & -.001 \\ 0 & 1 & 0 & 0 & 0 & -.007 & -.007 & -.007 & -.093 \\ 0 & 0 & 1 & 0 & 0 & -.007 & -.007 & -.093 & -.007 \\ 0 & 0 & 0 & 1 & 0 & -.007 & -.093 & -.007 & -.007 \\ 0 & 0 & 0 & 0 & 1 & -.093 & -.007 & -.007 & -.007 \end{array}\right)$$

E [mH]	fCI	Δ_{HF}	Δ_{DOCI} (MO)	Δ_{DOCI}(OO)	Δ_{AP1roG}(OO)
STO-6G	-40190.572	80.110	55.106	17.457	17.464
6-31G	-40301.051	120.549	99.477	44.596	44.603

Richardson-Gaudin states as variational ansatz

- *non*-integrable DOCI Hamiltonian

$$H = \sum_{i=1}^{m} \varepsilon_i n_i + \sum_{ik} V_{ik} S_i^\dagger S_k$$

- RG as variational ansatz

$$E[g] = \langle RG(g)|H|RG(g)\rangle$$

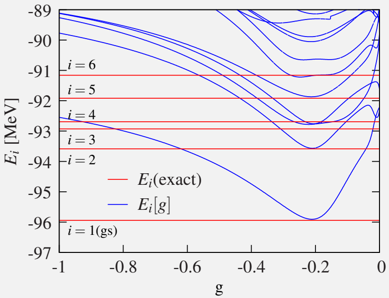
- $\min_g E[g]$ with integrability constraint

$$1 + \sum_{i=1}^{k} \frac{2 g d_i}{2\varepsilon_i - x_\alpha} - \sum_{\beta\neq\alpha}^{N} \frac{2g}{x_\beta - x_\alpha} = 0$$

- g defines a RG integrable model

example: nuclear Sn

- nuclear: collective pairs
- electronics: $(-)$ resonance pairs



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example: atomic Ne

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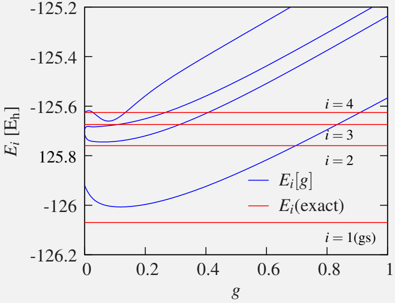
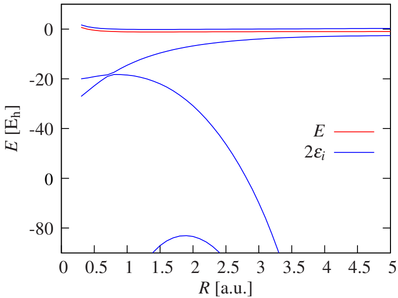


H_2 revisited

Geminal

- One to one correspondence

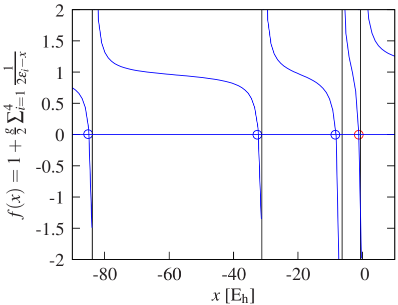
$$\sum_i \lambda_i S_i^\dagger |\theta\rangle = \sum_i \frac{S_i^\dagger}{2\varepsilon_i - E} |\theta\rangle$$



Integrability

- RG equation for 1 pair

$$1 + \frac{g}{2} \sum_i \frac{1}{2\varepsilon_i - E} = 0$$



variational quantum dots

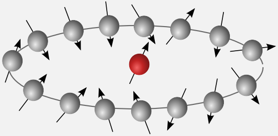
Central spin

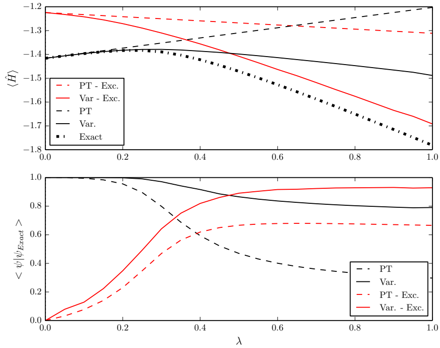
- Central Spin in $\vec{B}$-field

$$H_{CS} = BS_1^z + g\sum_{i\neq 1}\frac{\vec{S}_1\cdot\vec{S}_i}{\eta_1-\eta_i}$$

- Perturbation λ

$$H_{tot} = H_{CS} + \lambda\vec{S}_2\cdot\vec{S}_6$$





✍P Claeys, sdb, J-S Caux, & D Van Neck, *to be submitted*