

Richardson-Gaudin Wavefunctions for Strong Correlation

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Weak and Strong Correlation

Weak correlation

- Dispersion effects
- For molecules: one resonance structure
- HOMO-LUMO gap large compared with electronic repulsion

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Any system far from a mean-field of electrons (aufbau). Try to subdivide effects and treat correctly at the mean-field level.

Mean-field approach

Weakly-correlated:

$$|\Psi\rangle = |\text{HF}\rangle + \sum_{i,a} C_{i,a} |\Phi_i^a\rangle + \sum_{ij,ab} C_{ij,ab} |\Phi_{ij}^{ab}\rangle + \dots$$

Series “converges” provided that Hartree-Fock is a reasonable approximation to the exact result.

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- Productive to expand in seniority
- Solve seniority problems individually
- Start with **weakly-correlated pairs** rather than electrons

Seniority and DOCI

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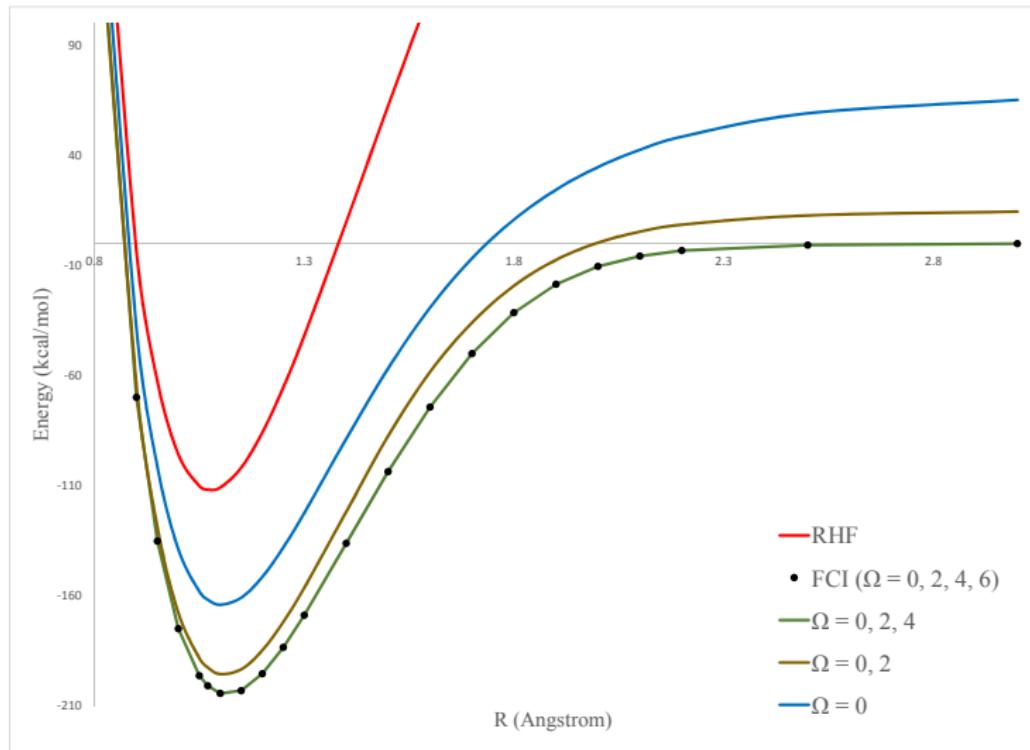
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$$\Omega = 0$$

$$\Omega = 2$$

$$\Omega = 4$$

- Seniority, Ω : the number of unpaired electrons of a given MO diagram
- Doubly-Occupied Configuration Interaction: DOCI, all diagrams with seniority zero
- Pair mean-fields have DOCI as best possible case



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In one spatial orbital, can make / remove pairs:

$$S^+ = a_\uparrow^\dagger a_\downarrow^\dagger, \quad S^- = a_\downarrow a_\uparrow, \quad S^z = \frac{1}{2} (a_\uparrow^\dagger a_\uparrow + a_\downarrow^\dagger a_\downarrow - 1)$$

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Extends to any number of spatial orbitals cleanly:

$$S_i^+ = a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger, \quad S_i^- = a_{i\downarrow} a_{i\uparrow}, \quad S_i^z = \frac{1}{2} (a_{i\uparrow}^\dagger a_{i\uparrow} + a_{i\downarrow}^\dagger a_{i\downarrow} - 1)$$

$$[S_i^+, S_j^-] = 2\delta_{ij} S_i^z, \quad [S_i^z, S_j^\pm] = \pm \delta_{ij} S_i^\pm$$

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- Richardson-Gaudin (RG) states: $G_a^\dagger = \sum_i \frac{S_i^+}{u_a - \varepsilon_i}$
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Occupied-Virtual separation type:

- GVB/PP: $G_a^\dagger = S_a^+ - S_{a+M}^+$
- APSG: $G_a^\dagger = S_a^+ + \sum_{b \in \mathcal{A}} g_{ab} S_b^+$
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Geminal wavefunction \approx Natural-Orbital functionals.

Explicit AGP and APSG

Implicit RG states and APIG

Richardson-Gaudin states

$$\hat{H}_{BCS} = \frac{1}{2} \sum_i \varepsilon_i \hat{n}_i - \frac{g}{2} \sum_{ij} S_i^+ S_j^-$$

Competition between **aufbau filling** and **pair scattering**.

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So $|\{u\}\rangle$ a solution provided garbage disappears, or

$$\frac{2}{g} + \sum_i \frac{1}{u_a - \varepsilon_i} + \sum_{b \neq a} \frac{2}{u_b - u_a} = 0.$$

Variational Program

Use RG states to approximate energy of Coulomb Hamiltonian \hat{H}_C

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- $\{\varepsilon\}, g$ define reduced BCS Hamiltonian
- Solve Richardson's equations for $\{u\}$
- Construct (normalized)

$$\gamma_i = \langle \{u\} | \hat{n}_i | \{u\} \rangle$$

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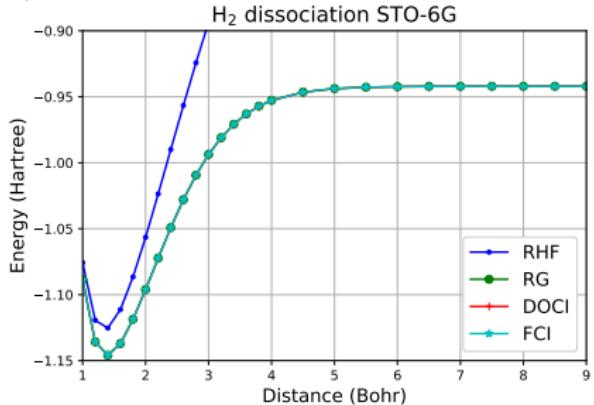
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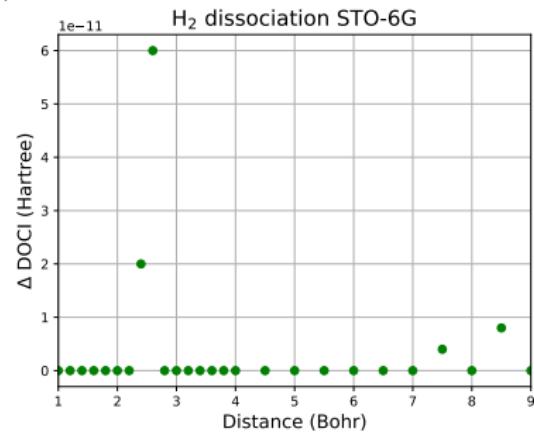
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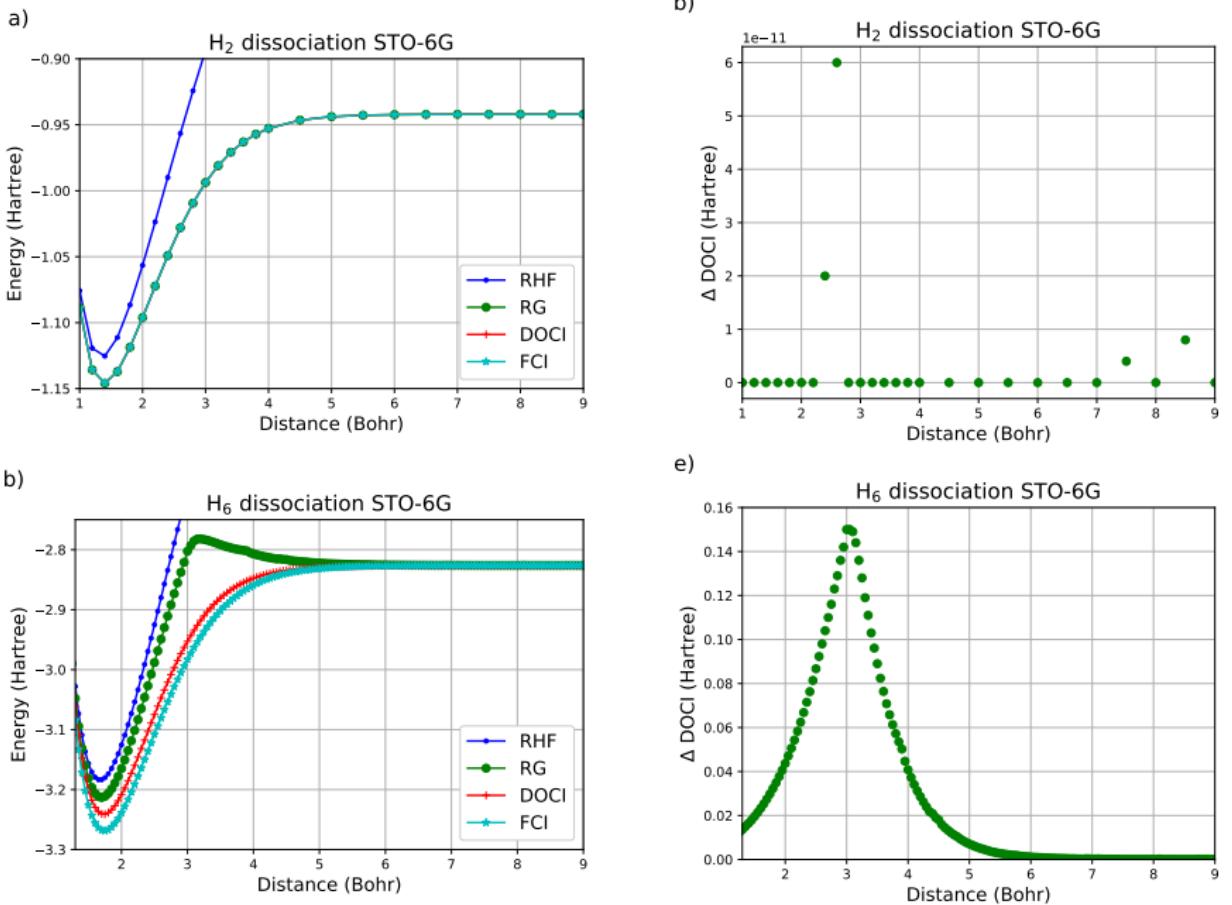
- **System:** $\{\varepsilon\}, g$
- **States:** $\{u\} \approx$ pair energies

a)



b)





APIG scalar products

$$\langle \{h\} | \{g\} \rangle = \sum_{\mathcal{P}} \prod_{P \in \mathcal{P}} \Gamma(\{h\}_P \cup \{g\}_P)$$

Sums of all possible rank-q contractions:

$$\Gamma(h_{a_1}, \dots, h_{a_q}, g_{b_1}, \dots, g_{b_q}) = (-1)^{(q-1)} q! (q-1)! \sum_i h_{a_1}^i \dots h_{a_q}^i g_{b_1}^i \dots g_{b_q}^i$$

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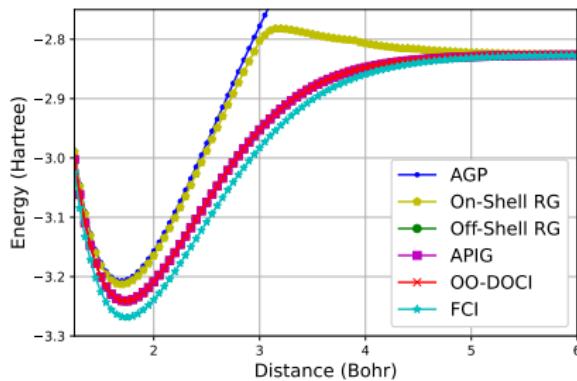
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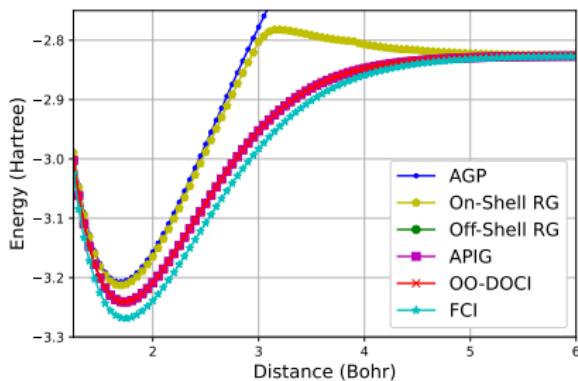
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APSG Sparsity: only diagonal rank-1 contractions are non-zero

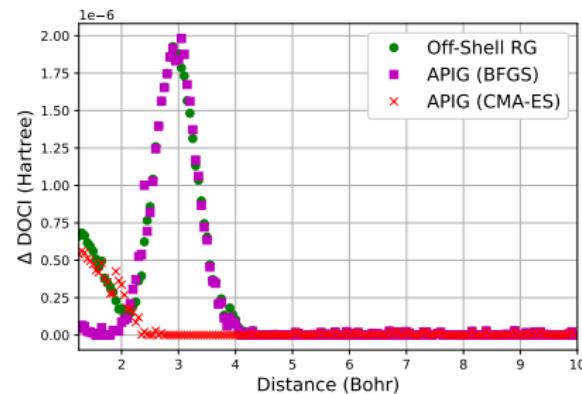
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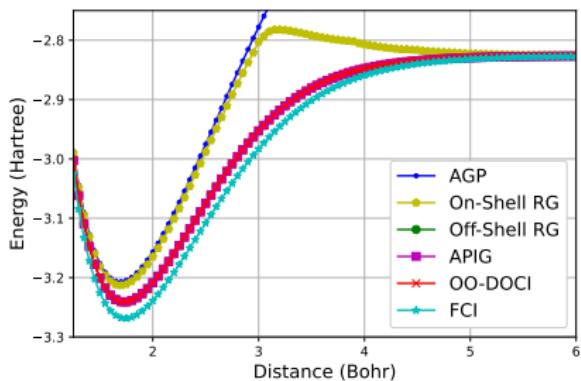
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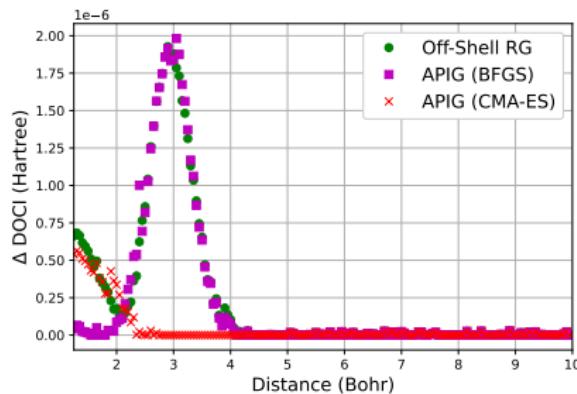
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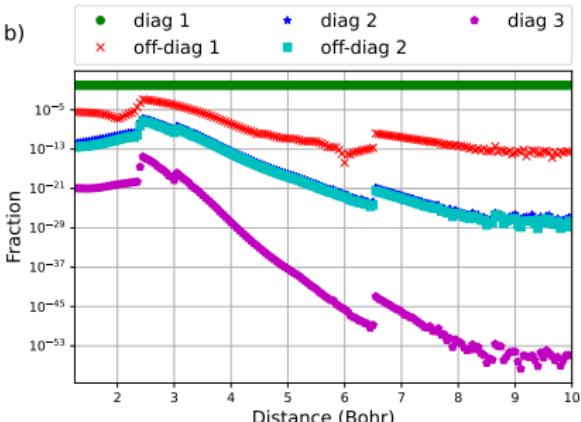
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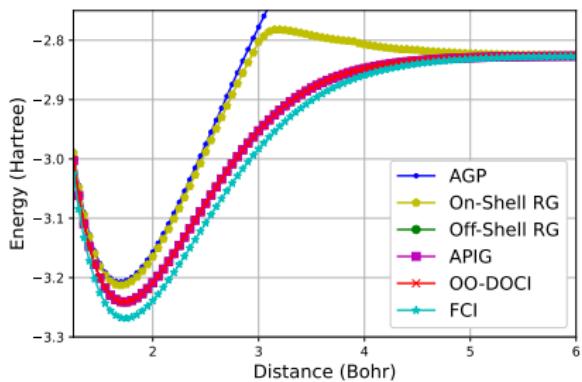
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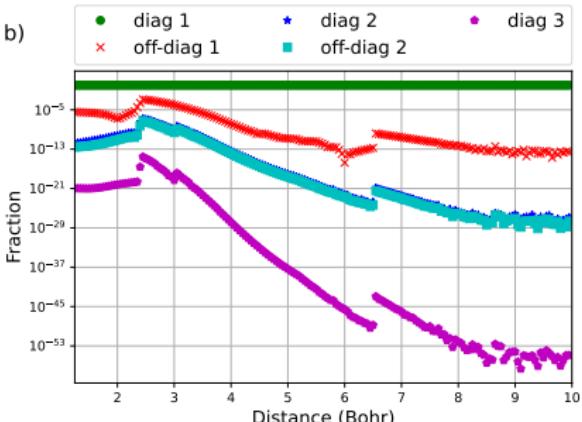
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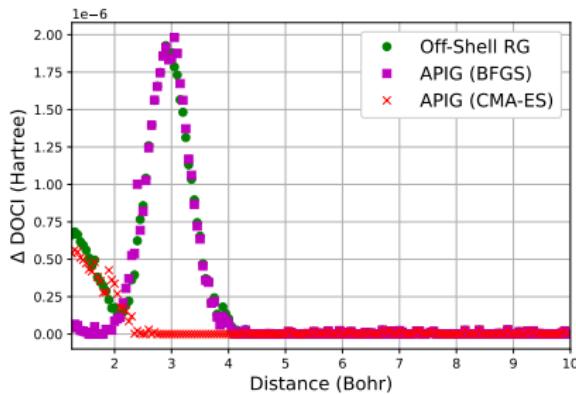
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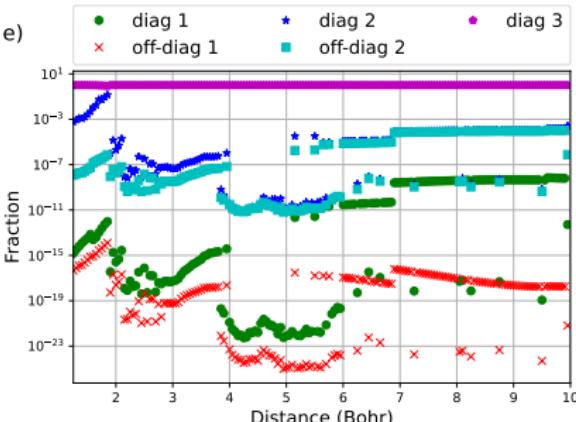
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RDM elements require computing rapidities $\{u\}$

$$\frac{2}{g} + \sum_i \frac{1}{u_a - \varepsilon_i} + \sum_{b(\neq a)} \frac{2}{u_b - u_a} = 0$$

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Use variables U_i , then root-find a Lagrange interpolation polynomial for $\{u\}$

$$U_i = \sum_a \frac{g}{\varepsilon_i - u_a}, \quad 0 = U_i^2 - 2U_i - g \sum_{k(\neq i)} \frac{U_k - U_i}{\varepsilon_k - \varepsilon_i}$$

Equations are solved by adiabatic evolution from $g = 0$

$$0 = U_i(U_i - 2)$$

Solutions at $g = 0$ are Slater determinants labelled by occupations and **evolve uniquely**. Unambiguous to label states based on $g = 0$, e.g.
111000, 110100, ..., 000111

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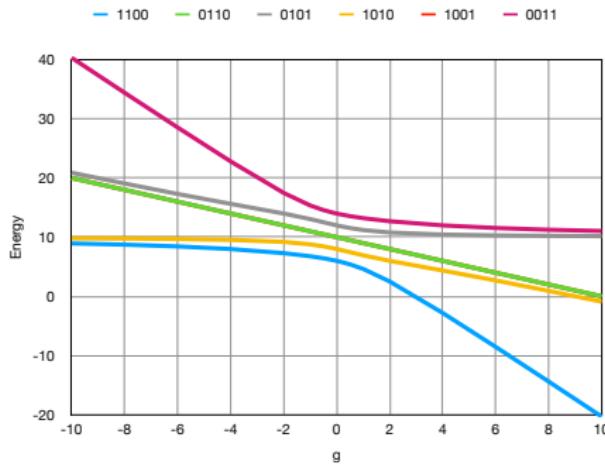
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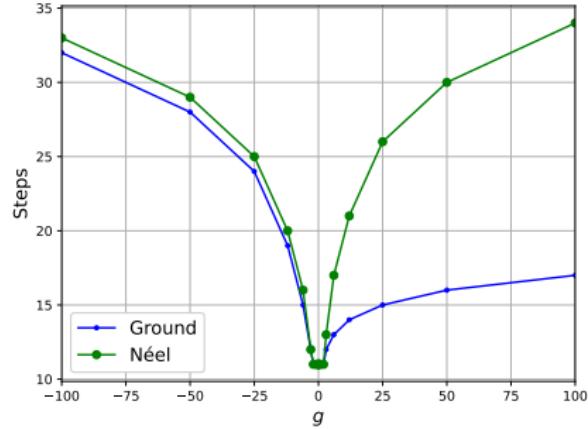
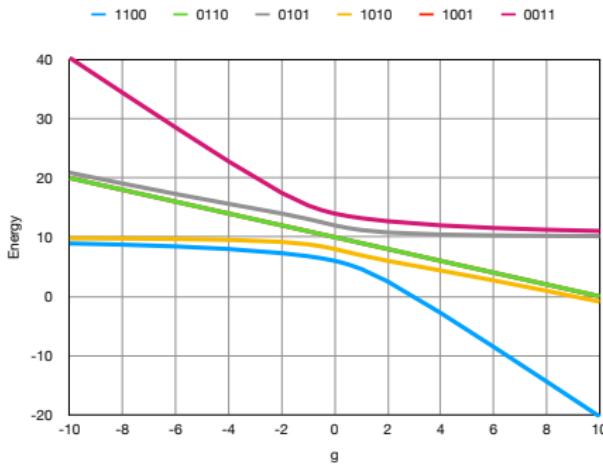
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RDM elements now only require variables U_i .



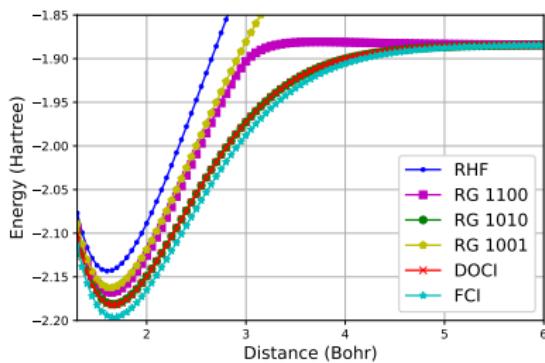


After assigning occupations at $g = 0$, dynamic g -step approach:

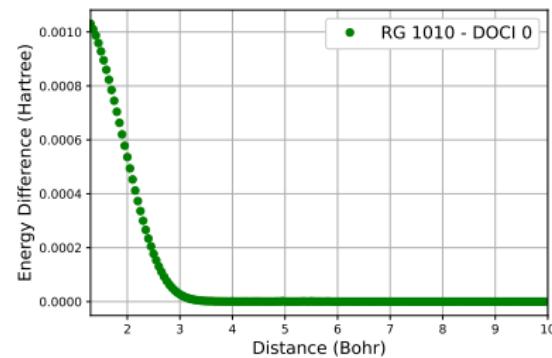
- Attempt large step with a Taylor series
- Reject, and retry with half-step if terms in series grow
- Newton-Raphson solve
- Reject, and retry if norm of $\{U\}$ changes by more than threshold

Number of steps required grows only **logarithmically** with g .

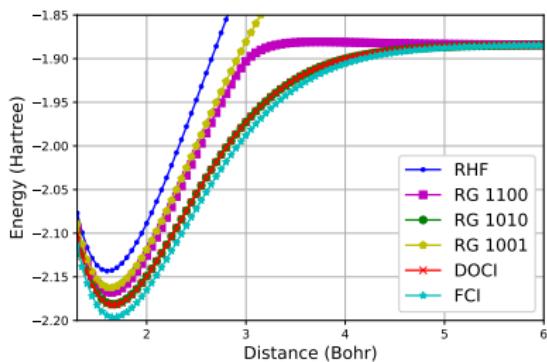
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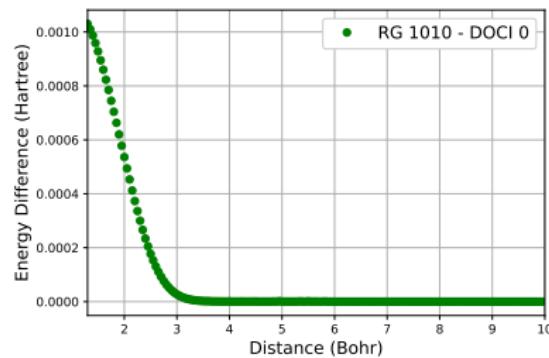
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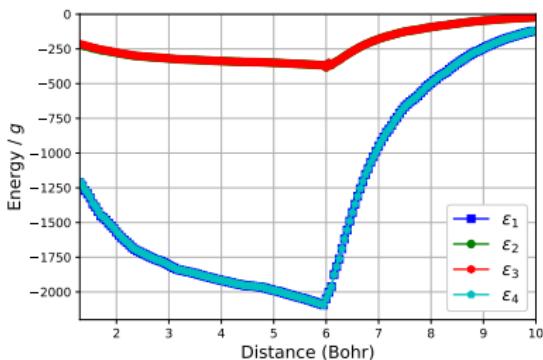
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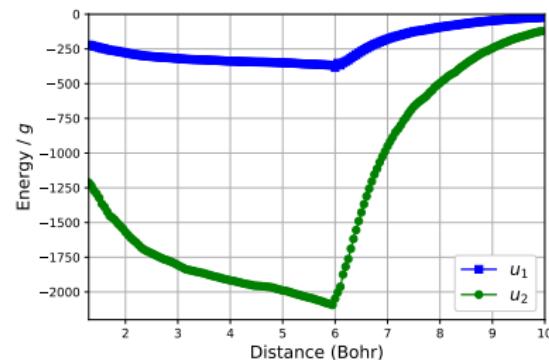
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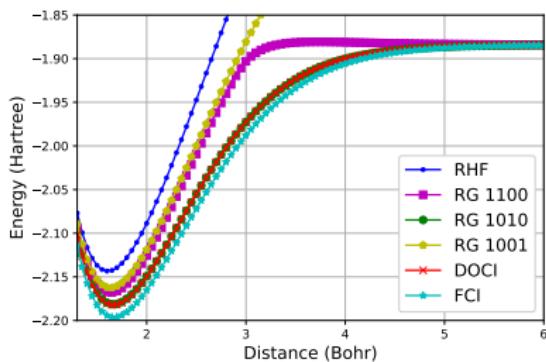
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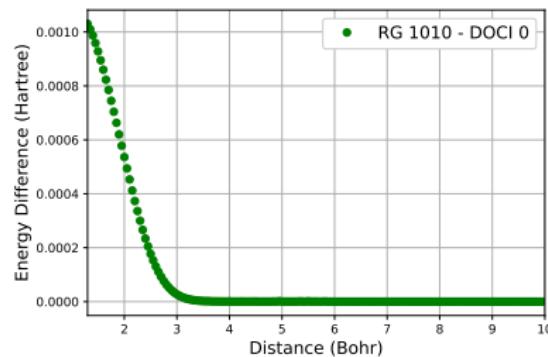
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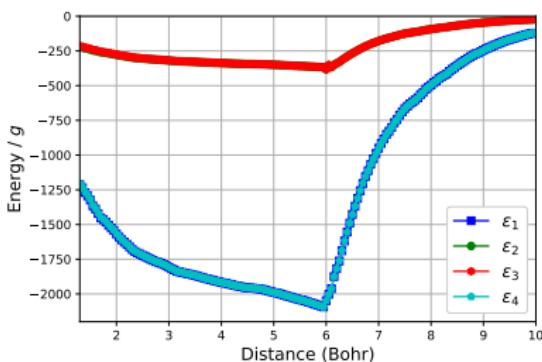
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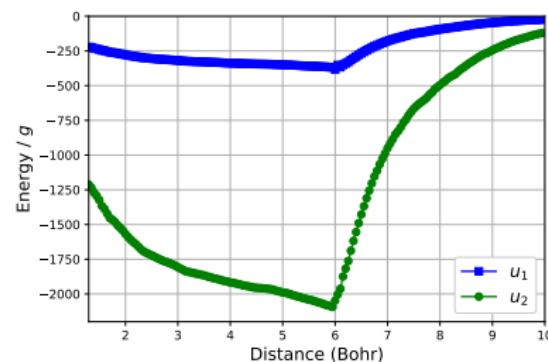
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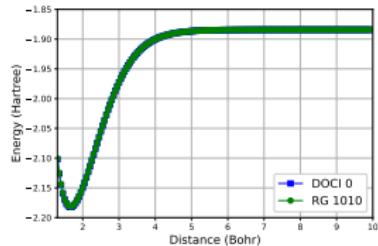


RG 1010 smoothly transitions from **RHF + pairs** to **GVB**

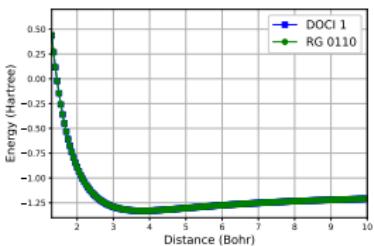
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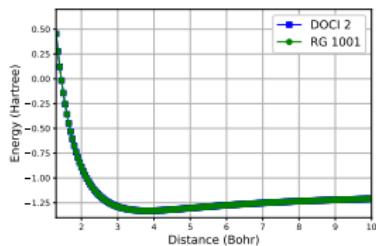
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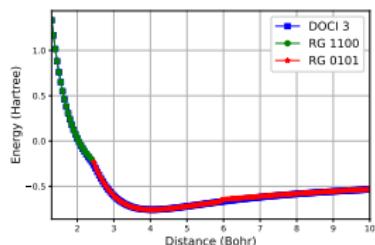
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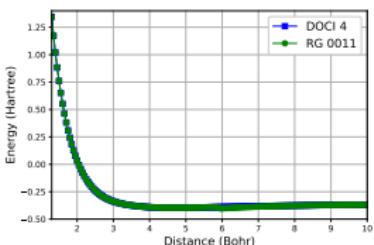
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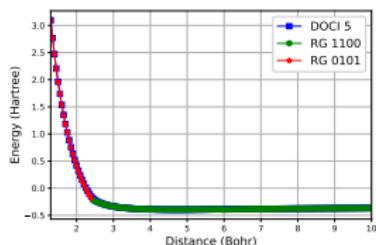
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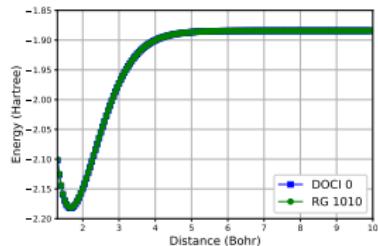


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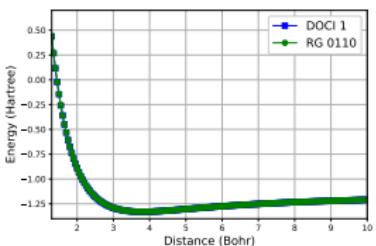


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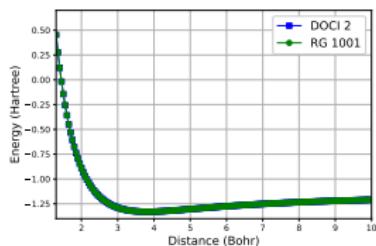
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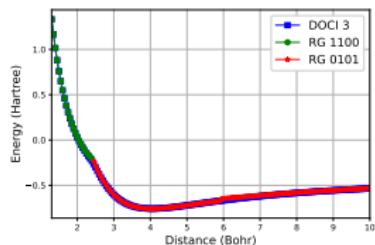
b)



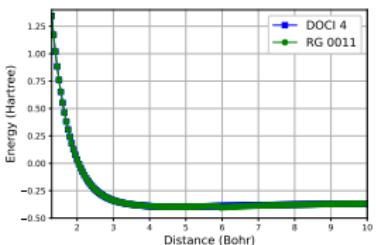
c)



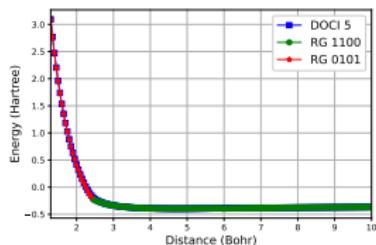
d)



e)



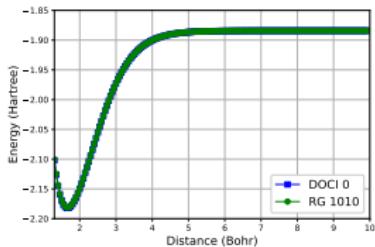
f)



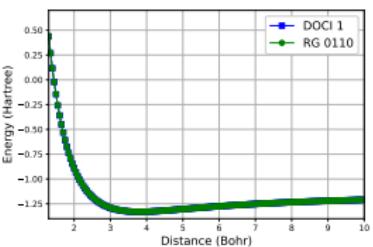
- The RG states **are** the DOCI states: non-interacting RG pairs is the physical picture

With $\{\varepsilon\}$ and g found for 1010 state, compute all other RG states.

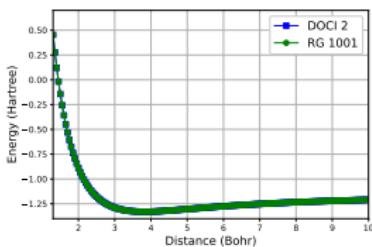
a)



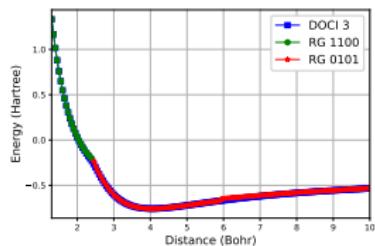
b)



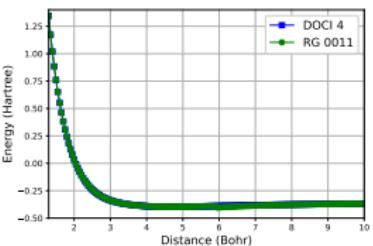
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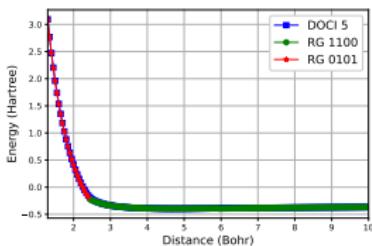
d)



e)

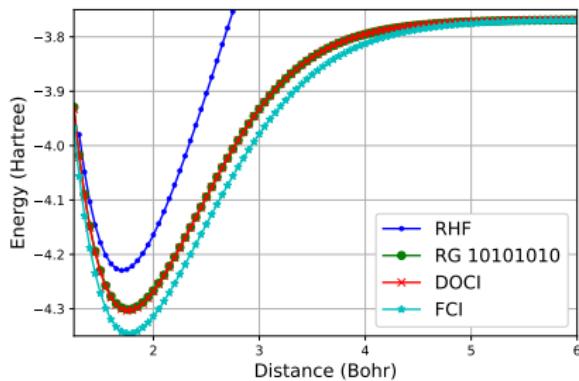


f)

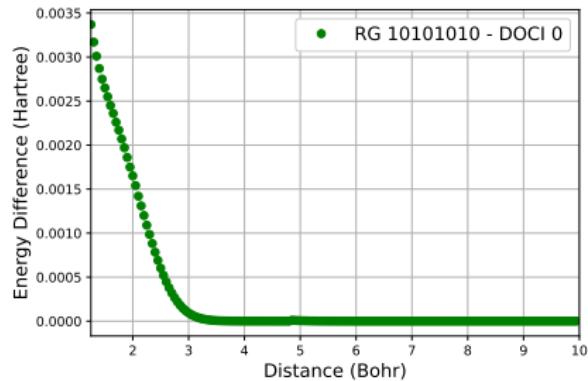


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- Correct description of excited states requires OO for each state...

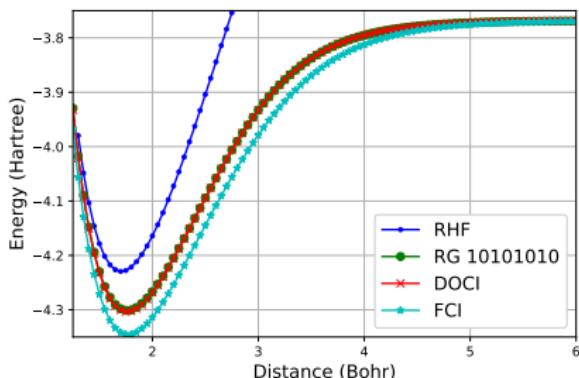
a)



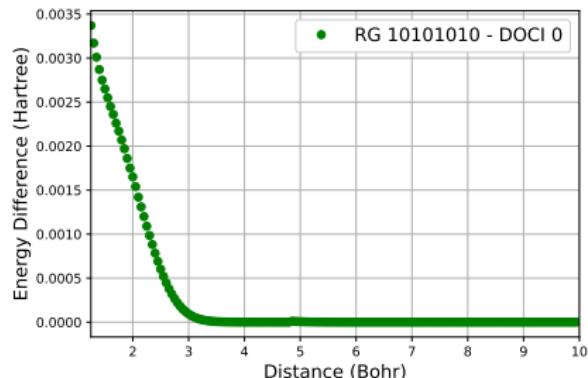
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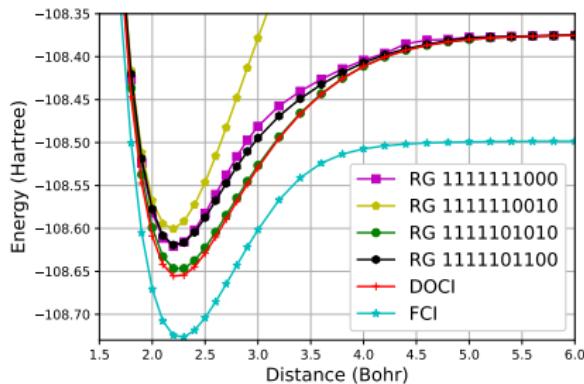
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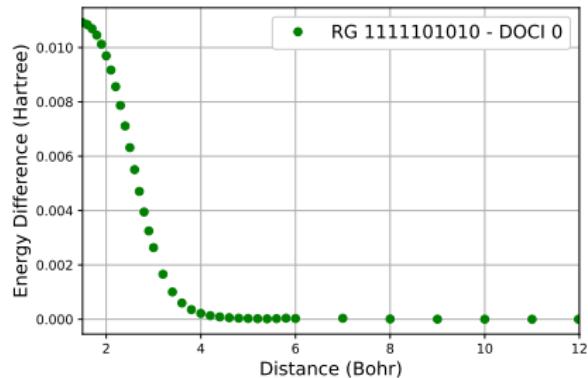
b)



a)



b)



More than one RG state

Can compute matrix elements between RG eigenvectors:

- Each state parametrized by distinct solution of $\{u\}$
- Transition matrix elements require determinants (but less clean)
- Analogue of aufbau principle for RG states
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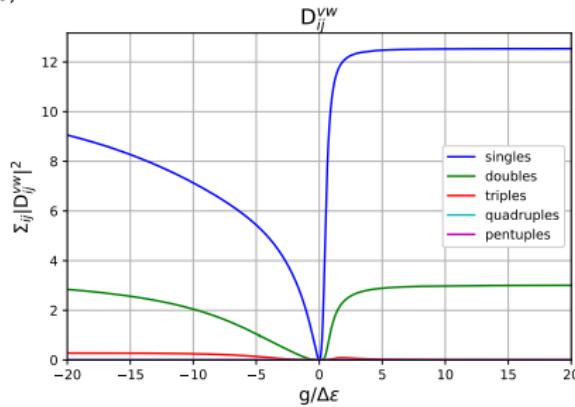
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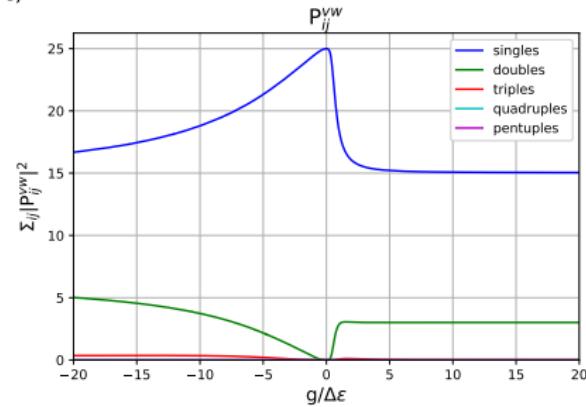
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- Complete set of eigenvectors
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- Choosing the correct RG state
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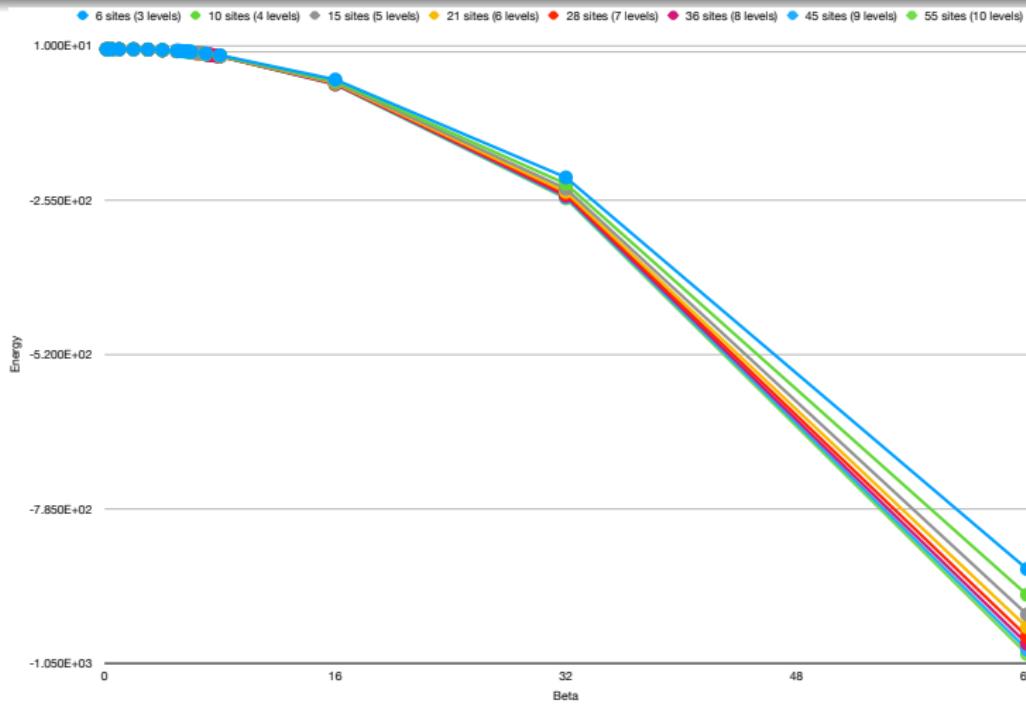
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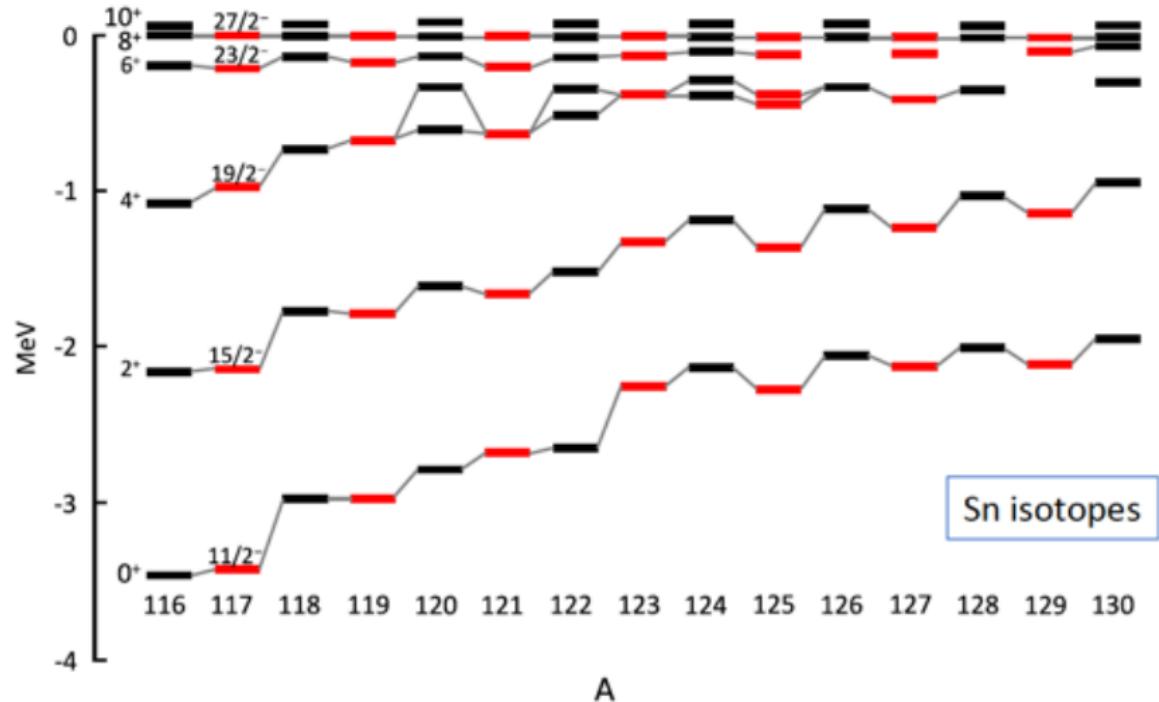
Machinery to employ RG states as a basis is not difficult!

More than 1 RG state required



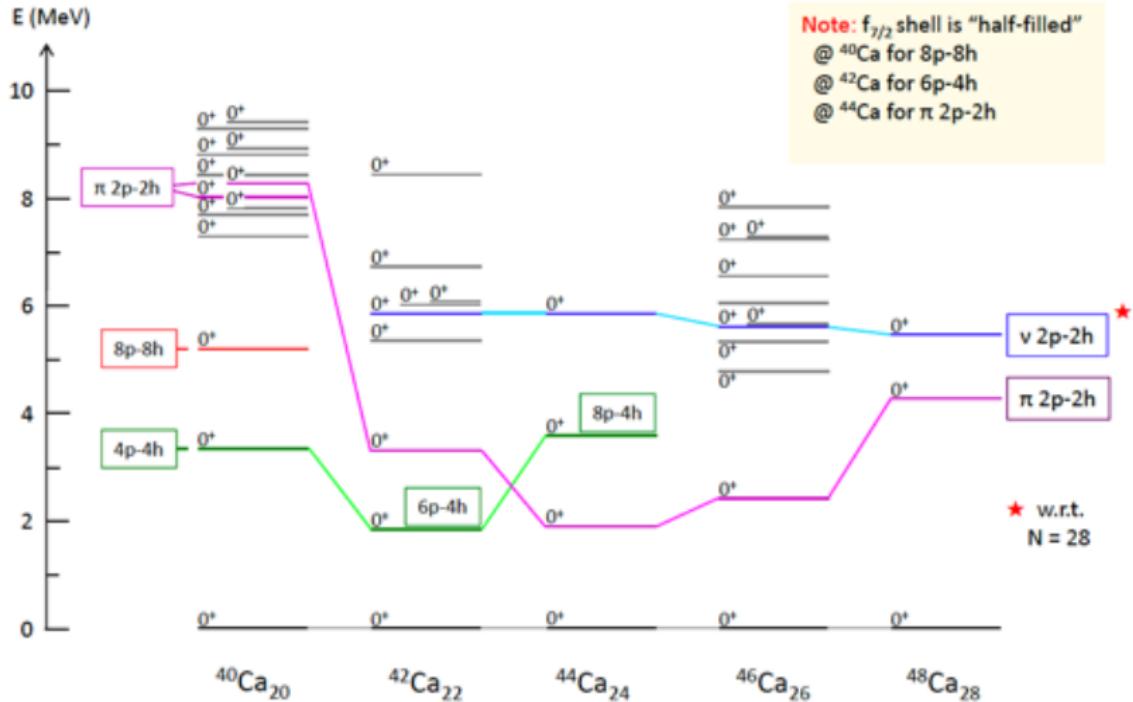
$$\hat{H} = \sum_i \eta_i \hat{n}_i + \sum_{ij} V_{ij}(\beta^2) S_i^+ S_j^-$$

More than 1 RG state required



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More than 1 RG state required



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- Daniel Fillion
- Hubert Fortin
- Marianne Gratton
- Meriem Khalfoun



We are looking for PhD students!
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