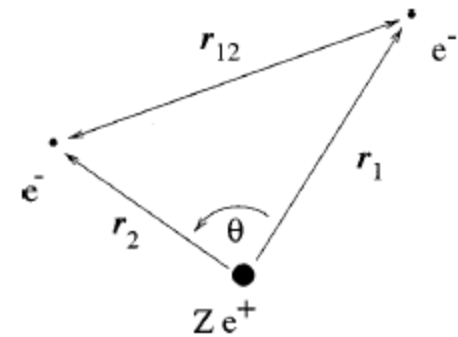
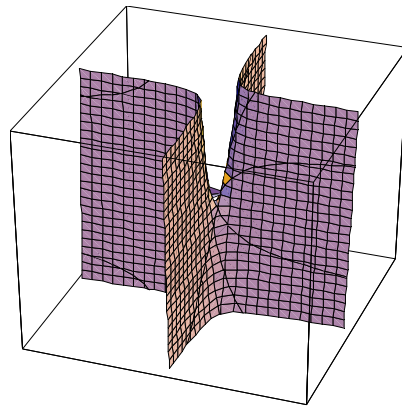




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Boundary-condition-determined wave functions (and their nodal structure) for few-electron atomic systems



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Critical stability V (Erice) 2008



Numbers and insight

- There is no shortage of accurate calculations for few-electron systems

$-2.90372437703411959831115924519440444669690537$ a.u.

Helium atom (Nakashima and Nakatsuji JCP 2007)

- *However...*

“The more accurate the calculations became, the more the concepts tended to vanish into thin air “

(Robert Mulliken)



The curse of Ψ_T

- Currently Quantum Monte Carlo (and quantum chemistry in general) uses moderately large to extremely large expansions for Ψ
- Can we ask for both **accurate** and **compact** wave functions?



VMC: Variational Monte Carlo

- Use the Variational Principle

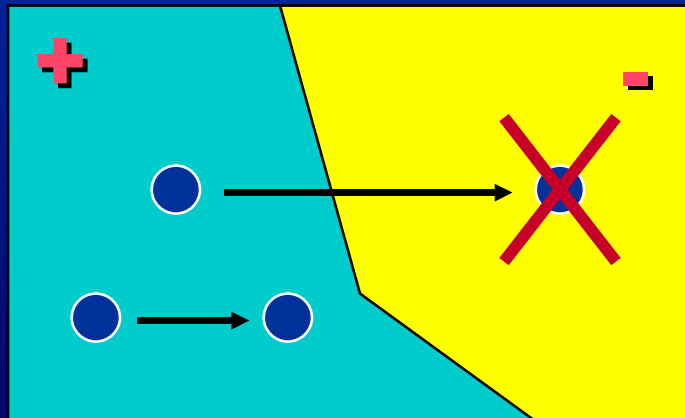
$$\langle H \rangle = \frac{\int \Psi(R) H \Psi(R) dR}{\int \Psi^2(R) dR} \geq E_0$$

- Use Monte Carlo to estimate the integrals
 - **Complete** freedom in the choice of the trial wave function
 - Can use interparticle distances into Ψ
 - But It depends **critically** on our skill to invent a good Ψ



QMC: Quantum Monte Carlo

- Analogy with diffusion equation
- Wave functions for fermions have nodes
- If we knew the *exact nodes* of Ψ , we could **exactly simulate** the system by QMC
- The *exact* nodes are unknown. Use approximate nodes from a **trial Ψ** as boundary conditions





Long term motivations

- In **QMC** we only need the zeros of the wave function, not what is in between!
- A stochastic process of diffusing points is set up using the nodes as boundary conditions
- The exact wave function (for that boundary conditions) is **sampled**
- We need ways to **build good approximate nodes**
- We need to study **their mathematical properties** (poorly understood)



Convergence to the exact Ψ

- We must include the correct analytical structure

Cusps: $\Psi(r_{12} \rightarrow 0) \approx 1 + \frac{r_{12}}{2}$ $\Psi(r \rightarrow 0) \approx 1 - Zr$

QMC OK

3-body coalescence and logarithmic terms: **QMC OK**

Tails and fragments: **Usually neglected**



Asymptotic behavior of Ψ

■ Example with 2-e atoms $H = \frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}$

$$H \xrightarrow{r_2 \rightarrow \infty} \frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z-1}{r_2}$$

$$\Psi \xrightarrow{r_2 \rightarrow \infty} \phi_0(r_1) r_2^{(Z-1)/\beta - 1} e^{-\beta r_2} \quad \beta = \sqrt{2E_I}$$

$\phi_0(r_1)$ is the solution of the 1 electron problem



Asymptotic behavior of Ψ

- The usual form

$$\Psi = \phi(r_1)\phi(r_2)$$

$$\Psi = e^{-a(r_1+r_2)}$$

does **not** satisfy the asymptotic conditions

$$\Psi(r_2 \rightarrow \infty) \rightarrow \phi_0(r_1)\phi(r_2)$$

$$\Psi(r_1 \rightarrow \infty) \rightarrow \phi(r_1)\phi_0(r_2)$$

⋮

{⋮⋮⋮

⋮

A closed shell determinant has the **wrong** structure

$$\Psi = \phi(r_1)\phi(r_2) + \phi(r_2)\phi(r_1)$$



Asymptotic behavior of Ψ

- In general $\Psi_0^N \xrightarrow{r_1 \rightarrow \infty} r_1^{a_1} (1 + c_1 r_1^{-1} + O(r_1^{-2})) e^{-r_1/b_1} Y_{ll}^{ml}(r_1) \Psi_0^{N-1}(2, \dots, N)$

Recursively, fixing the cusps, and setting the right symmetry...

$$\Psi = \hat{A}(f_1(1) f_2(2) \dots f_N(N) \Theta_N) e^U$$

Θ_N = spin function, e^U = correlation factor

Each electron has its own orbital, **Multideterminant (GVB) Structure!**



PsH – Positronium Hydride

- A wave function with the correct asymptotic conditions:

$$\Psi(1,2,e^+) = (1 + \hat{P}_{12})\Psi(H^-) f(r_{e^+}) \Psi(Ps) g(r_{1e^+})$$

Type	Energy (hartree)
SCF	-0.6669
VMC single term	-0.7723
Hylleraas 12 terms	-0.7742
VMC single term	-0.7774
CI 95324 configurations	-0.7867761
MRCI 13230 configurations	-0.786782
Hylleraas 396 terms	-0.788951
ECG 1600 terms	-0.7891965536
Hylleraas 5741 terms	-0.7891967
DMC	-0.78918(5)
DMC	-0.78915(4)
VMC single term	-0.786073(6)



Basis

- In order to build **compact** wave functions we used orbital functions where **the cusp** and the **asymptotic behavior** are decoupled

$$1s = e^{\frac{ar+br^2}{1+r}} \quad \begin{array}{l} \rightarrow e^{ar} \quad r \rightarrow 0 \\ \rightarrow e^{br} \quad r \rightarrow \infty \end{array}$$



2-electron atoms

$$\Psi = (1 + \hat{P}_{12}) \exp\left(\frac{a_1 r_1 + b_1 r_1^2}{1 + r_1}\right) \exp\left(\frac{a_2 r_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{dr_{12}}{1 + er_{12}}\right)$$

Tails OK



$$\Psi = (1 + \hat{P}_{12}) \exp\left(\frac{-Zr_1 + b_1 r_1^2}{1 + r_1}\right) \exp\left(\frac{-Zr_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + er_{12}}\right)$$

Cusps OK – 3 parameters



$$\Psi = (1 + \hat{P}_{12}) \exp(-Zr_1) \exp\left(\frac{-Zr_2 + b_2 r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + er_{12}}\right)$$

Fragments OK – 2 parameters (coalescence wave function)



Z dependence

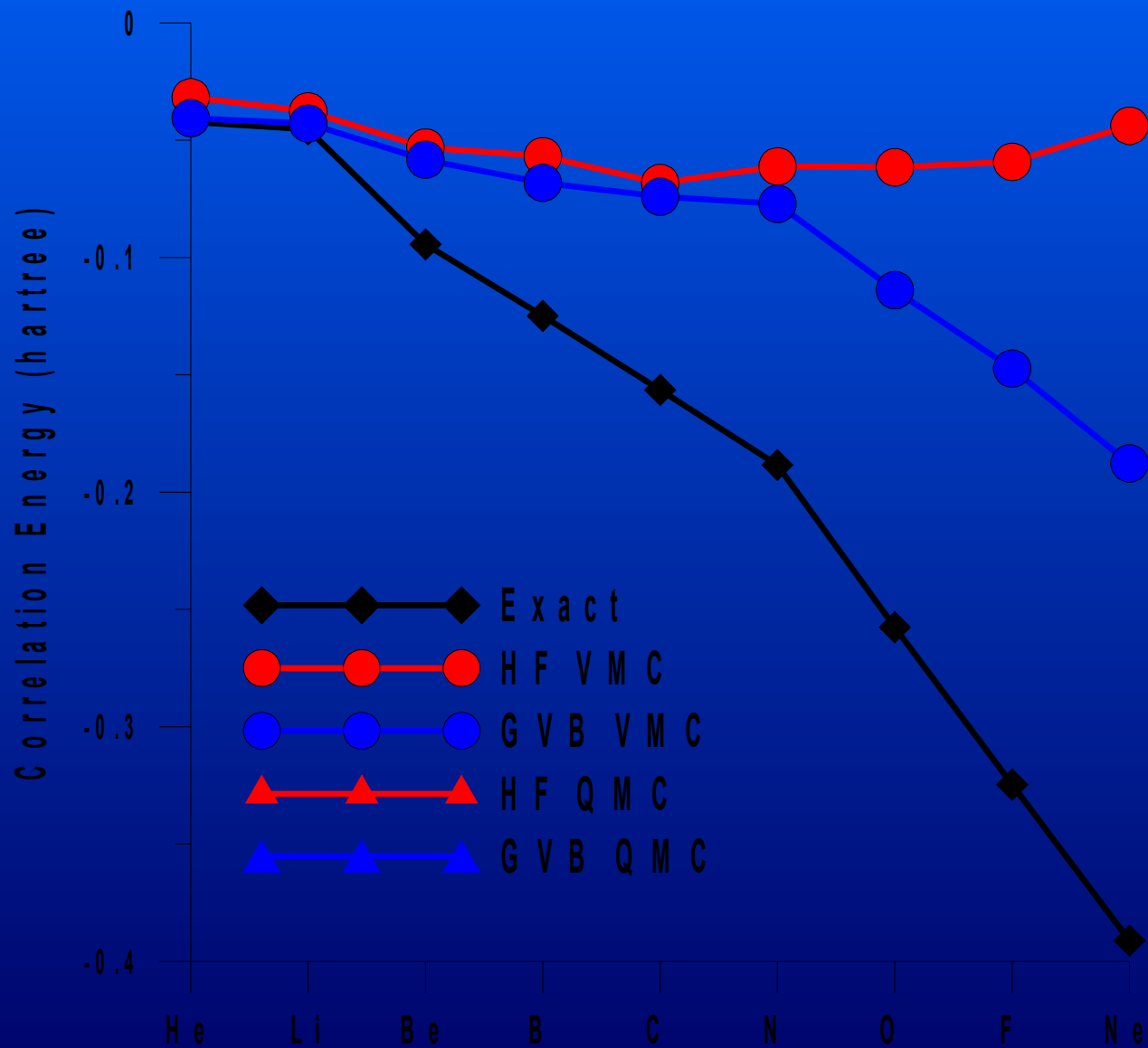
- Best values around for compact wave functions
- D. Bressanini and G. Morosi J. Phys. B 41, 145001 (2008)
- We can write a general wave function, with Z as a parameter and fixed constants k_i

$$\Psi(1,2|Z) = (1 + \hat{P}_{12}) \exp\left(\frac{-Zr_1 + Z k_2 r_1^2}{1 + r_1}\right) \exp\left(\frac{-Zr_2 + (k_3 + Z k_4) r_2^2}{1 + r_2}\right) \exp\left(\frac{r_{12}/2}{1 + Z k_1 r_{12}}\right)$$

- Tested for Z=30
- Can we use this approach to larger systems?
Nodes for QMC become crucial

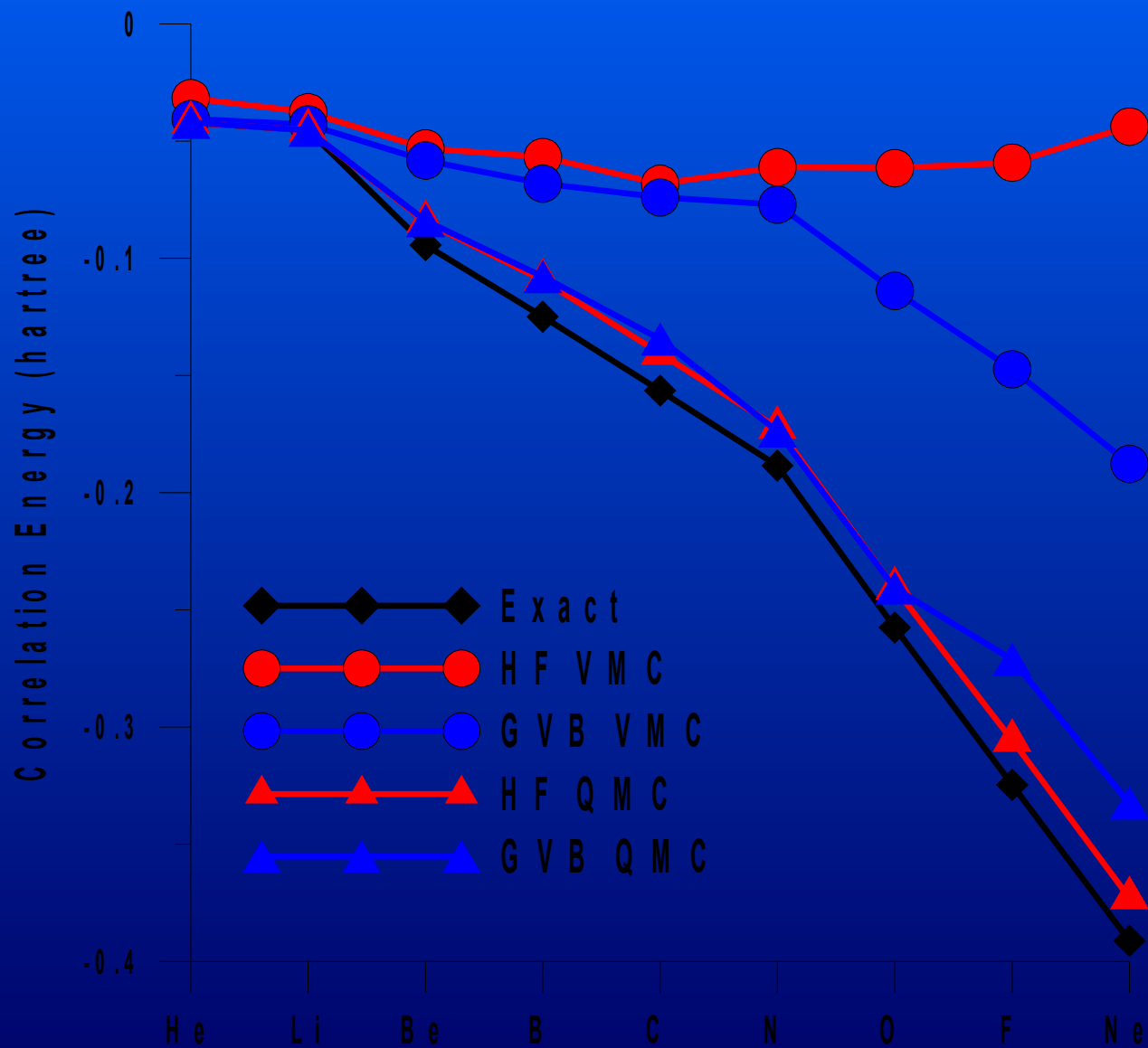


For larger atoms ?





GVB Monte Carlo for Atoms





Nodes does not improve

- The wave function can be improved by incorporating the known analytical structure... with a small number of parameters
- ... but the nodes do not seem to improve
- Was able to prove it mathematically **up to N=7** (Nitrogen atom), but it seems a general feature

$$\blacksquare E_{\text{VMC}}(\Psi_{\text{RHF}}) > E_{\text{VMC}}(\Psi_{\text{GVB}})$$

$$\blacksquare E_{\text{DMC}}(\Psi_{\text{RHF}}) = E_{\text{DMC}}(\Psi_{\text{GVB}})$$

Is there anything “critical”
about the nodes of critical
wave functions?



Critical charge Z_c

- 2 electrons:
$$H = \frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}} \quad \lambda = \frac{1}{Z}$$
- Critical Z for binding $Z_c = 0.91103$
- Ψ_c is square integrable $\|\Psi_c\|_2 < +\infty$
- $\lambda < 1$: infinitely many discrete bound states
- $1 \leq \lambda \leq \lambda_c$: only one bound state
- All discrete excited state are absorbed in the continuum **exactly** at $\lambda = 1$
- Their Ψ become more and more diffuse

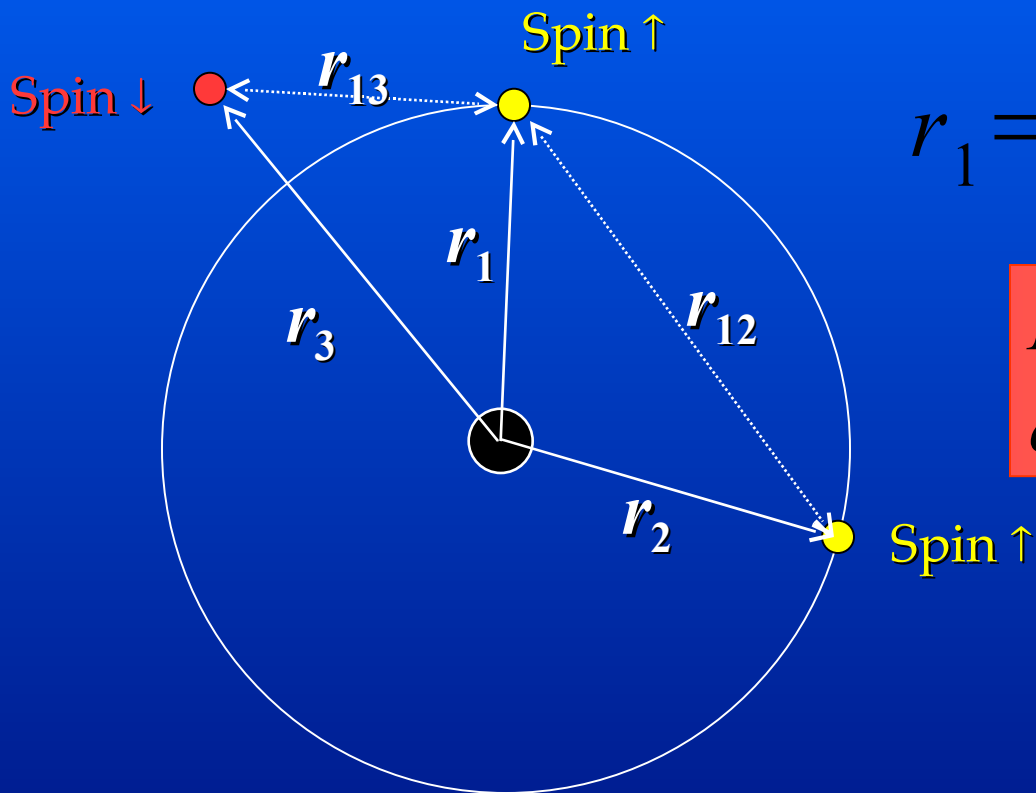


Critical charge Z_c

- N electrons atom
- $\lambda < 1/(N-1)$ infinite number of discrete eigenvalues
- $\lambda \geq 1/(N-1)$ finite number of discrete eigenvalues
- $N-2 \leq Z_c \leq N-1$ $\|\Psi_Z\|_2 \rightarrow \infty$
- $N=3$ “Lithium” atom $Z_c \cong 2$. As $Z \rightarrow Z_c$ $\|\Psi_c\|_2 < +\infty$
- $N=4$ “Beryllium” atom $Z_c \cong 2.85$ As $Z \rightarrow Z_c$



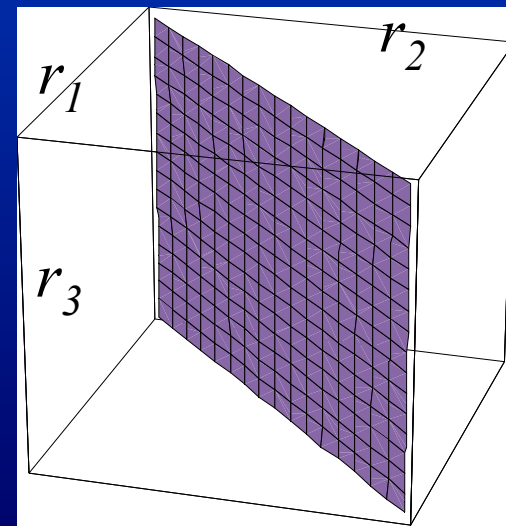
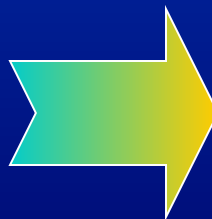
Lithium atom



$$r_1 = r_2 \Rightarrow \Psi_{\text{Hartree-Fock}} = 0$$

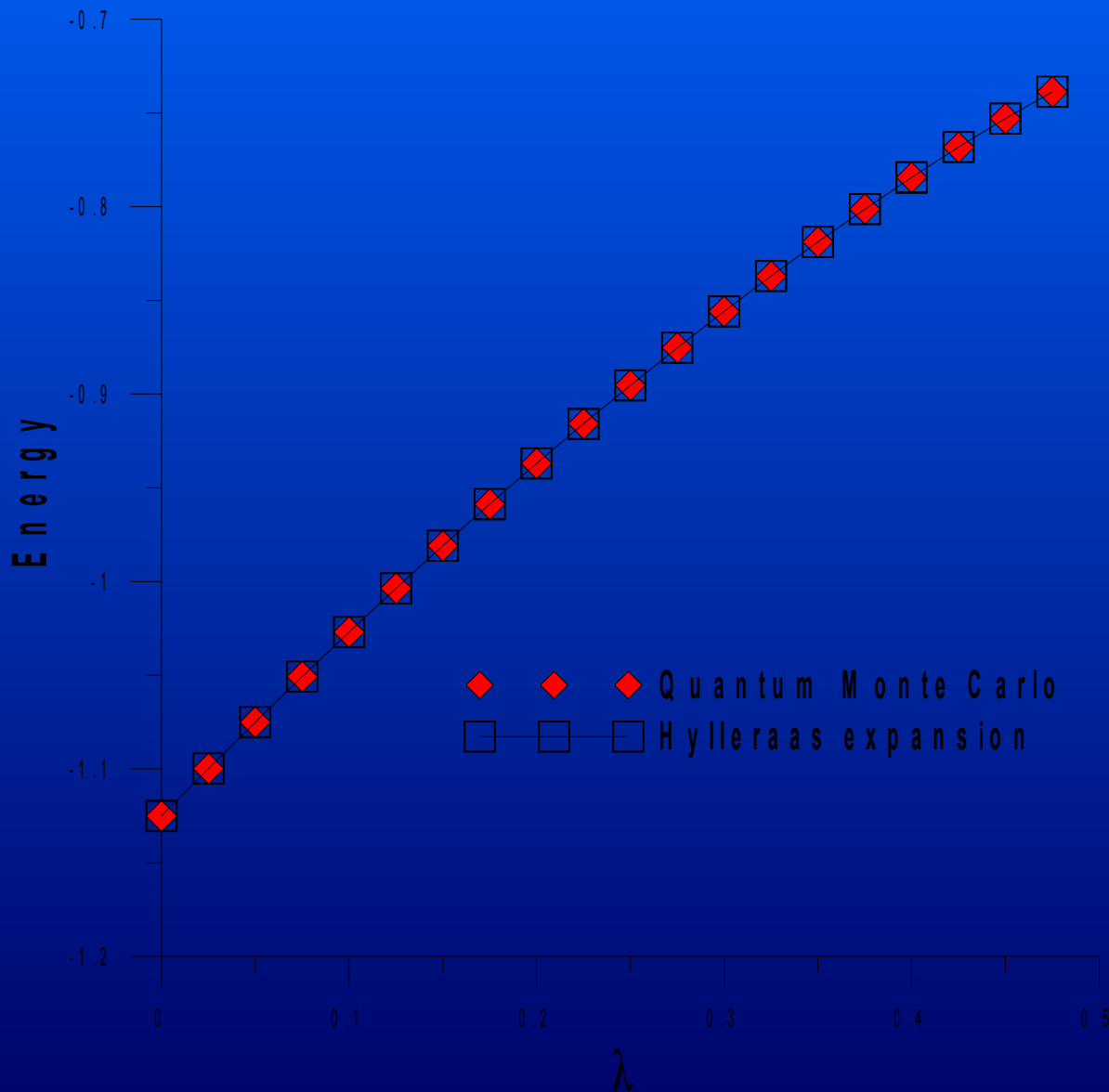
Is $r_1 = r_2$ the exact node of Lithium?

- Even the exact node seems to be $r_1 = r_2$, taking different cuts (using a very accurate Hylleraas expansion)





Varying Z: QMC versus Hylleraas



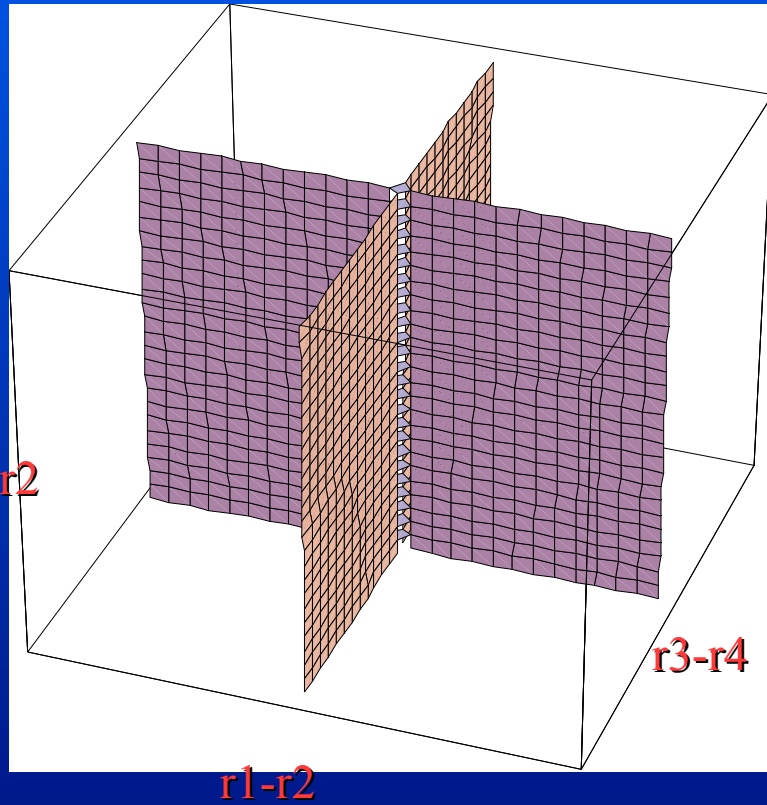
preliminary results

The node $r_1=r_2$ seems to be valid over a wide range of λ

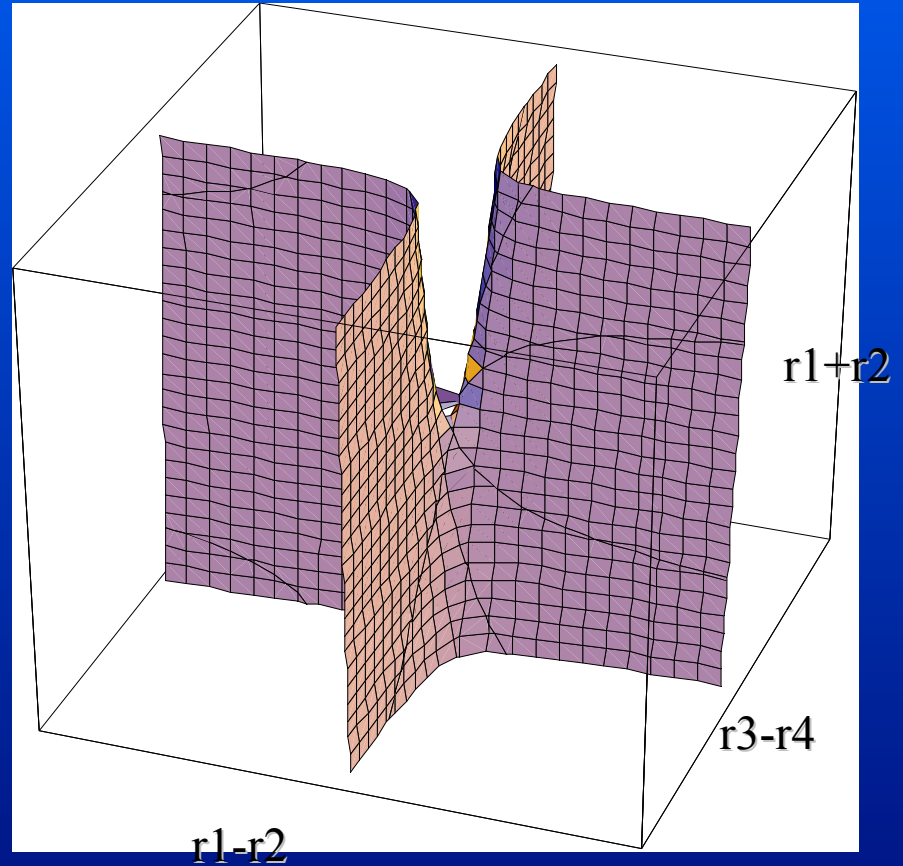
Up to $\lambda_c = 1/2$?



Be Nodal Topology



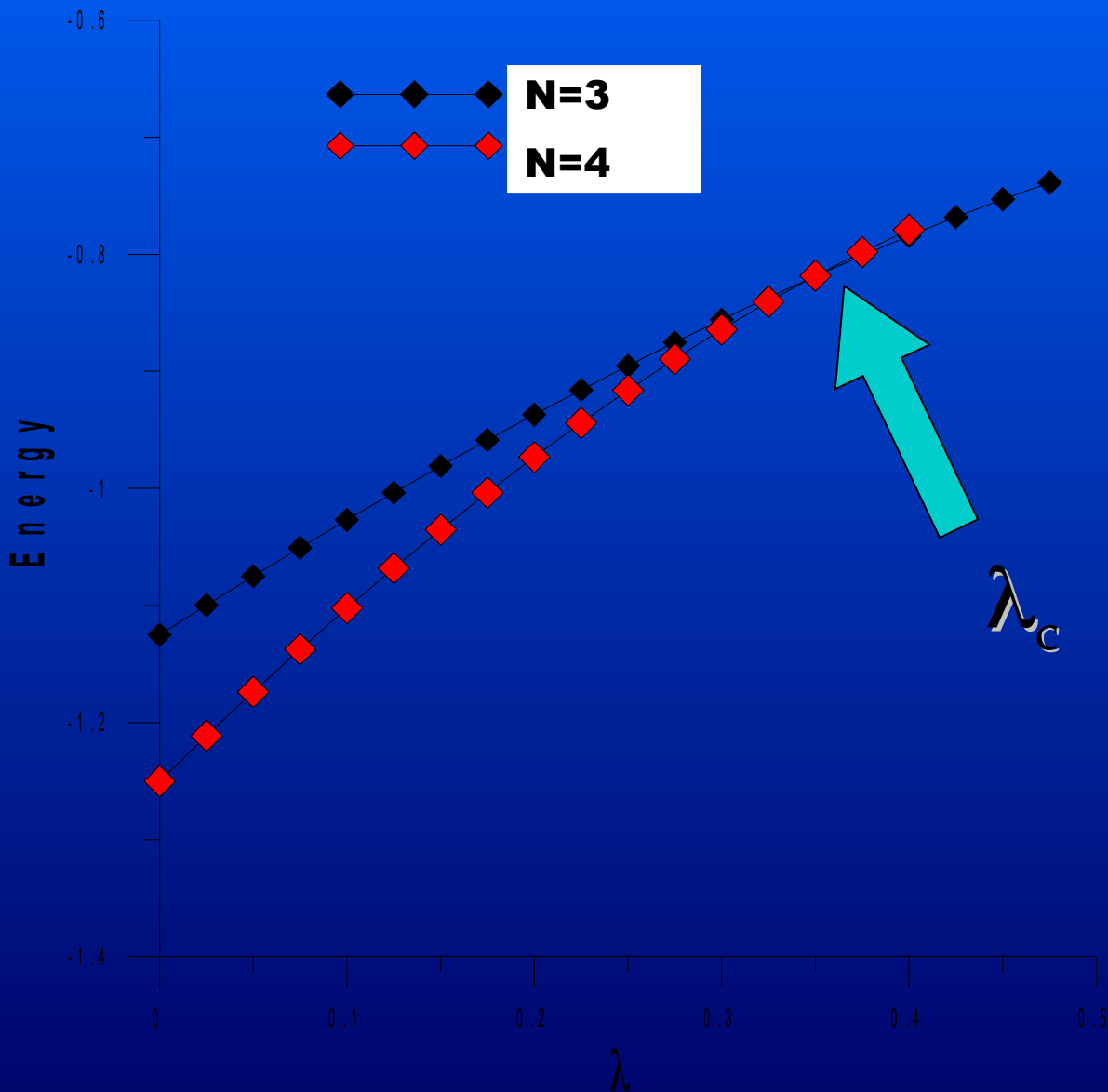
$$\Psi_{HF} = 0$$



$$\Psi_{Exact} = 0$$
$$\Psi = |1s^2 2s^2| + c |1s^2 2p^2|$$

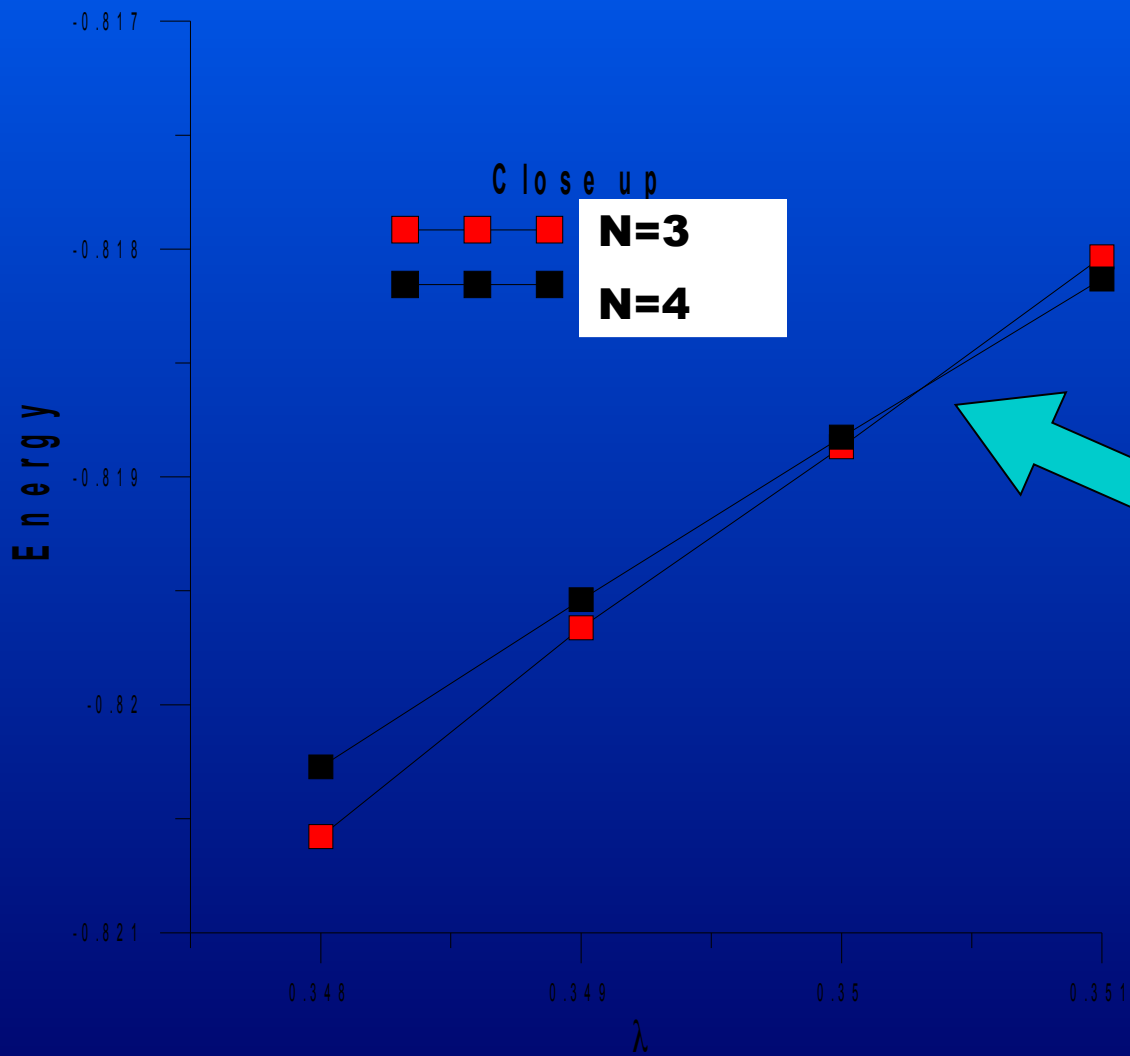


N=4 critical charge





N=4 critical charge

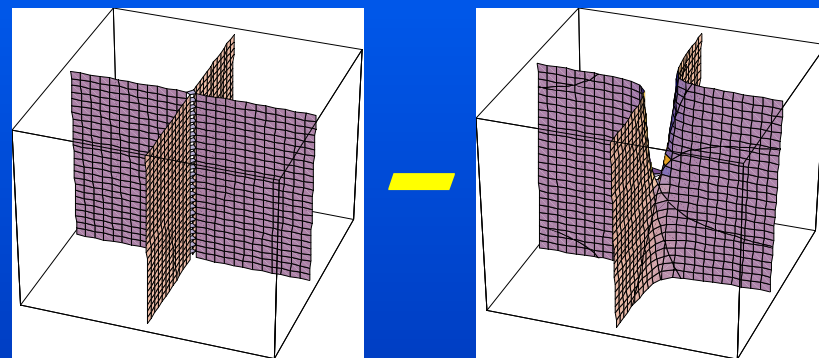


$\lambda_c \cong 0.3502$
 $Z_c \cong 2.855$

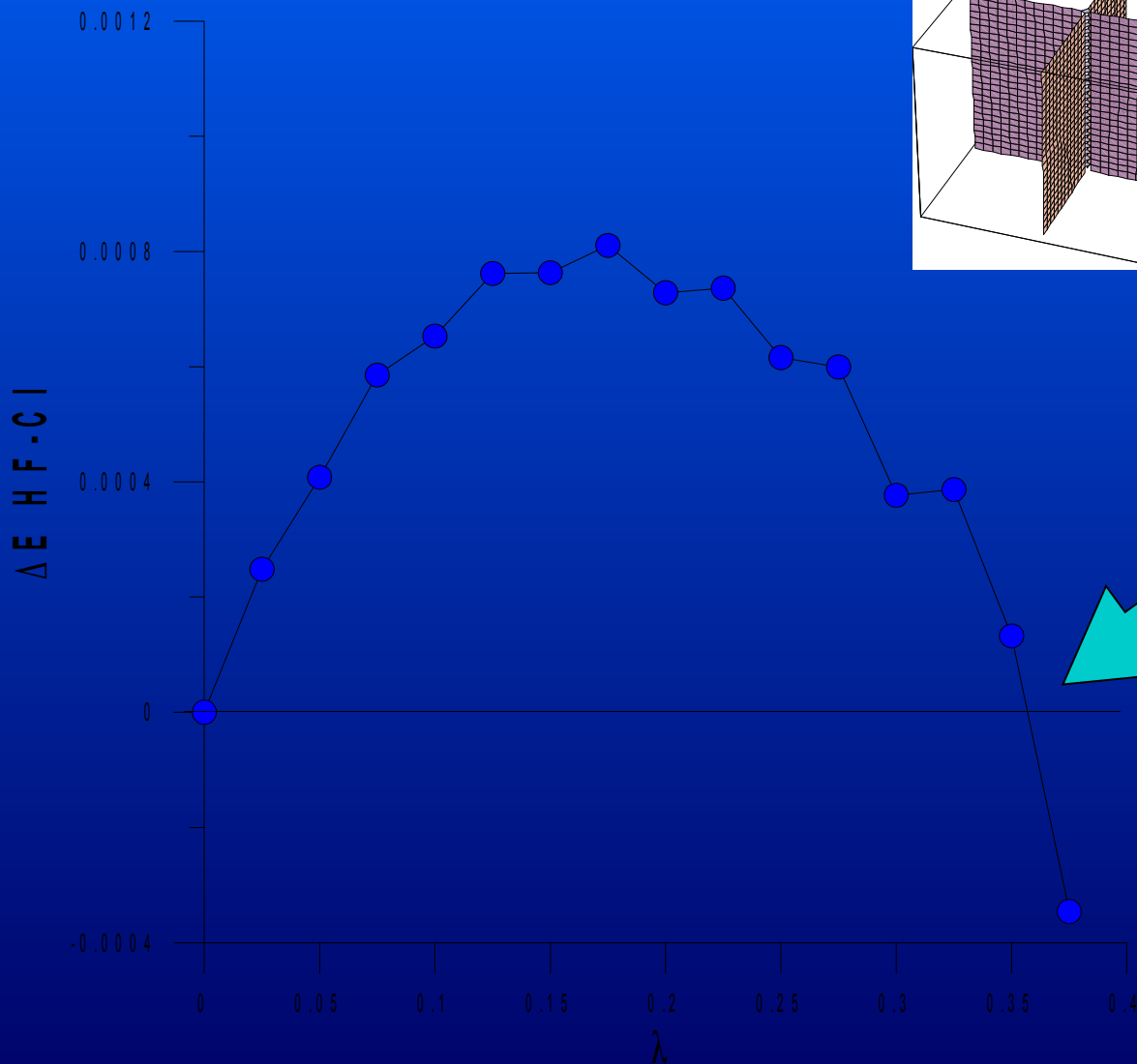
Z_c (Hogreve) $\cong 2.85$



N=4 critical charge node



preliminary results



very close to $\lambda_c = 0.3502$

Critical Node very close to
 $(r_1 - r_2)(r_3 - r_4) = 0$



The End



*Take a look at **your** nodes*