Quantum Monte Carlo calculations on Rydberg states and transition metal oxides

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QMC workshop, The Towler Institute, July 26 - August 2, 2008

Outline

- Few details of our quantum Monte Carlo methods
- Excited states: nodal domains
- Optimal nodes in fixed-node DMC
- vanadium oxides with QMC

DMC: Importance Sampling with Guide Function

guide function $\Phi_G(\mathbf{r})$ forces spatial and spin symmetry

$$f(\mathbf{r},\tau) := \Psi(\mathbf{r},\tau)\Phi_G(\mathbf{r})$$

Hamiltonian $\tilde{H} = \Phi_G H \Phi_G^{-1} - E_{\mathrm{ref}}$ (non-Hermitian)

Importance sampled DMC algorithm:

- *diffusion step*
- *drift step* towards large $|\Phi_G(\mathbf{r})|$
- *weight/branch step* with $e^{-(E_L(\mathbf{r})-E_{\mathrm{ref}})\tau}$

with *local energy*: $E_L(\mathbf{r}) = \dfrac{H\Phi_G(\mathbf{r})}{\Phi_G(\mathbf{r})}$

- Φ_G can statisfy (two-particle) cusp conditions ⇒ singularities vanish!
- Asymptotic ($\tau \to \infty$) probability density $f(\mathbf{r},\tau) \to \Phi_G(\mathbf{r})\Phi_0(\mathbf{r})$

Quantum Monte Carlo for Electron Structure

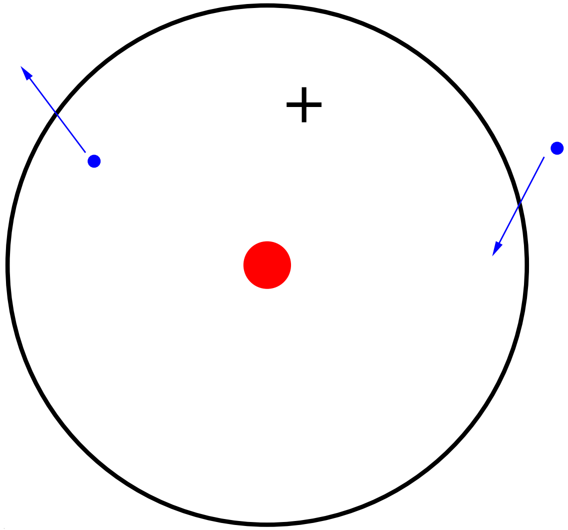
Pauli principle causes nodes in wave function: $\Psi(\mathbf{r}) = 0$

- Fermion sign problem!

example: exact nodes for ^{3}S He: $r_1 = r_2$

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

- note: orbital ansatz $\Psi = 1s^1 2s^1$ has *exact* nodes,
  no correlation effect on nodes: complicated wf but simple nodes!
- more exact nodes: Lubos Mitas and coworker



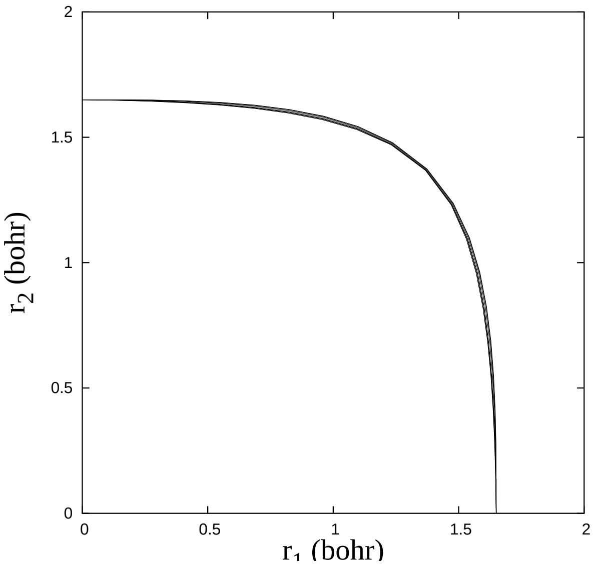
exact Helium nodes

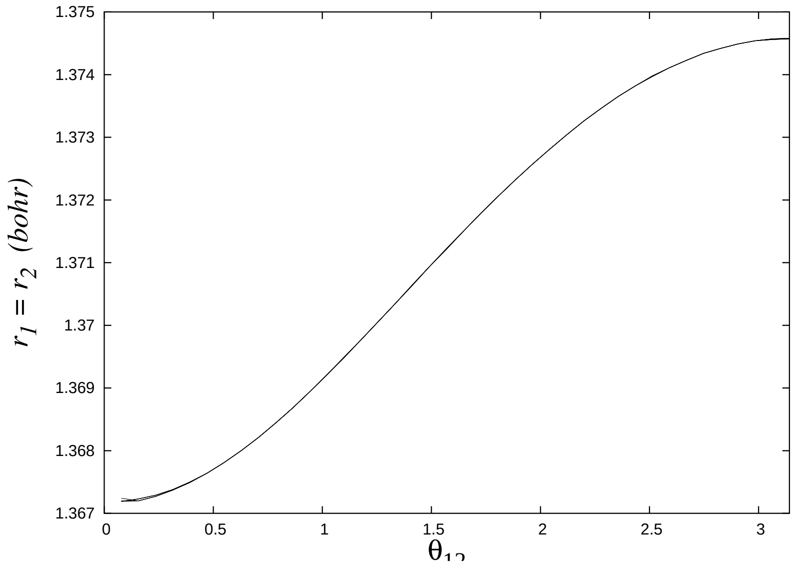
Similar for singlet states ^{1}S He?

- Is there a correlation effect on nodes, i.e. dependence on r_{12} or θ_{12}?
- High accuracy Hylleraas-CI wavefunctions indicate:
  no dependence on θ_{12} (Bressanini, Reynolds)

We find with very high accuracy (Frankowski-Pekeris basis):

- Small but significant dependence on θ_{12}:
  simple nodes, very weak correlation dependence





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[a] T.C. Scott, A. Lüchow, D. Bressanini, J.D. Morgan III, PRA 75,060101(R), (2007)

Quantum Monte Carlo for Electron Structure

- nodes are $3n-1$-dimensional hypersurfaces
- *fixed node approximation (FN-DMC):*
  use nodes from known functions (here: ab initio)
- usually: enforce nodes from guide function $\Phi_\mathsf{G} = \Phi_\mathsf{det} \mathsf{e}^\mathsf{U}$ then $\Psi(\tau)\Phi_\mathsf{G} \geq 0$ (probability density)
- FN-DMC solves Schrödinger equation with additional boundary condition *exactly*
- $\rightarrow$ *node location error*
- or: released-node methods

excited states with DMC: nodal domains

consequences of the fixed-node approximation:

- $3n-1$ dimensional nodal hypersurface partitions the space $\mathbb{R}^{3n}$ in disjoint domains $\{\Omega_j\}$
- FN-DMC means: Solving S.E. in one or more domains

$$\begin{aligned} H\Psi_0^{(j)}(\mathbf{r}) = E_0^{(j)}\Psi_0^{(j)}(\mathbf{r}) \quad &\text{for} \quad \mathbf{r} \in \Omega_j \\ \Psi_0^{(j)}(\mathbf{r}) = 0 \quad &\text{for} \quad \mathbf{r} \notin \Omega_j \end{aligned}$$

- *domain energies* $E_0^{(j)}$ are identical if domains Ω_j are related by permutation
- *Tiling theorem (Ceperley):* in exact ground state all domains are related by permutation
- spurious nodes: even in ground state e.g. through limited basis[a]
- excitation nodes: different domains Ω_j in excited states

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[a] J. Hachmann et al. (Handy group) CPL 392, 55 (2004)

Rydberg states with QMC

- generally:
    - the higher the excitation the more hydrogenic the Rydberg orbital becomes, even for molecules
    - HF or standard DFT virtual orbitals too diffuse
    - excited state calculations with QMC require guide functions with many Slater determinants
    - CASSCF-type calculations do not scale well and result in many determinants

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- here for low-lying Rydberg states:
  - we use (unoptimized) OSLHF Kohn-Sham orbitals:
    very efficient in QMC
  - triplet states: one determinant ($M_S = 1$)
  - singlet states: two determinants
  - large molecules possible both with OSLHF and QMC

OSLHF

- open shell localized Hartree-Fock (OSLHF) method
  - recent DFT method by Görling and Della Sala
  - self-interaction free method with exact exchange
  - proper description of open shell atoms and molecules
- here:
  - combination with Lee-Yang-Parr (LYP) correlation functional
  - calculations with standard cc-pVTZ basis set plus several diffuse functions (no ECP, but cusp corrected MOs)
  - bond centered diffuse functions for Rydberg character

Rydberg states: Carbon atom

excitation energies and singlet-triplet splittings in eV.

	OSLHF	*FN-DMC, simple*	*Expt*
^{3}P (2p3s)	7.71	7.716(4)	7.48
^{1}P (2p3s)	7.93	7.884(4)	7.68
^{3}P (2p4s)	9.90	9.815(5)	9.68
^{1}P (2p4s)	9.96	9.780(6)	9.71
^{3}P (2p5s)	10.65	10.505(5)	10.38
^{1}P (2p5s)	10.67	10.408(4)	10.40
^{3}P (2p6s)	10.99	10.803(7)	10.70
^{1}P (2p6s)	11.01	10.668(8)	10.71
2p3s	0.22	0.168(3)	0.20
2p4s	0.06	$-0.035(6)$	0.03
2p5s	0.03	$-0.096(4)$	0.01
2p6s	0.02	$-0.136(8)$	0.01

A. Bande, A. Lüchow, F. Della Sala, A. Görling, JCP 124, 114114 (2006).

nodal domains for C atom

analysis of nodal domains (not exhaustive) of C atom for current Slater determinants from OSLHF/LYP orbitals

- motivation: different domain energies? spurious nodes due to incomplete basis sets?
- finding nodal domains:
  FN-DMC runs started with one walker only in arbitrary positions
- importance of nodal domains:
  FN-DMC started with each walker of Ψ_T^2 VMC sample
- averaging electron coordinates in each block
- analysis for ground state and ^{1}P (2p6s) state

nodal domains for C atom

- ^{1}P (2p6s) Rydberg state: *domain energies* and topological characterization

	$E_{\text{FN-DMC}}$	spin up $\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle r_3 \rangle$	spin down $\langle r_4 \rangle$	$\langle r_5 \rangle$	$\langle r_6 \rangle$
Ω_1	−37.4378(5)	1.5	1.5	1.5	1.1	1.1	1.1
Ω_2	−37.4311(4)	43	1.5	0.3	1.1	1.1	1.1
Ω_3	−37.4280(3)	20	1.5	0.3	1.1	1.1	1.1
Ω_4	−37.4249(4)	10	1.5	0.3	1.1	1.1	1.1
Ω_5	−36.563(1)	35	1.4	0.3	38	1.0	0.7
Ω_6	−36.554(1)	46	1.4	0.3	30	1.4	0.3

energies in E_h and distances in bohr, individual standard deviations

- excitation nodes: different domain energies
- additionally spurious nodes: increase of FN-DMC excitation energy?
- standard DMC calculation (random initial sample) ends in Ω_1

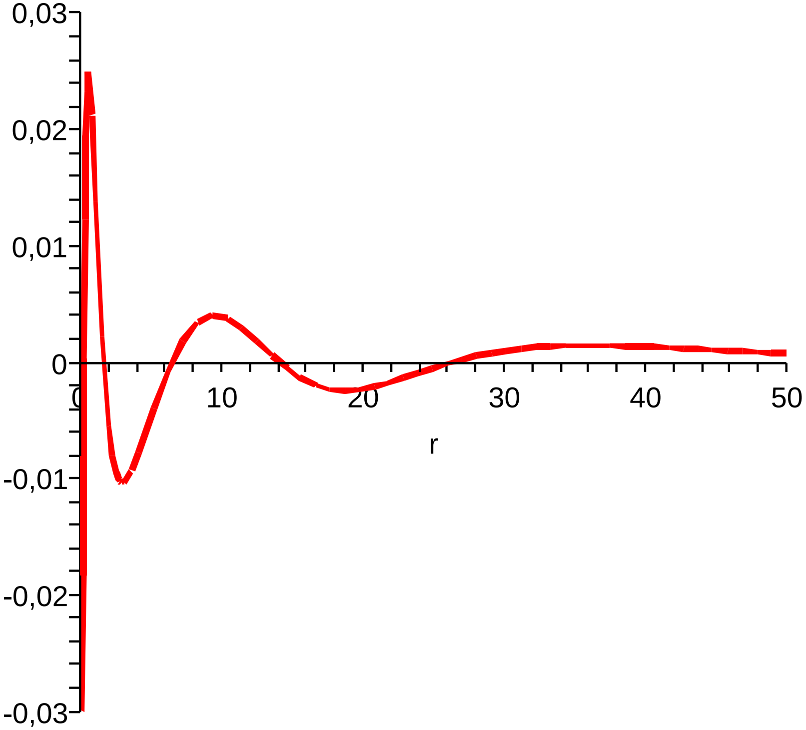
nodal domains for C atom

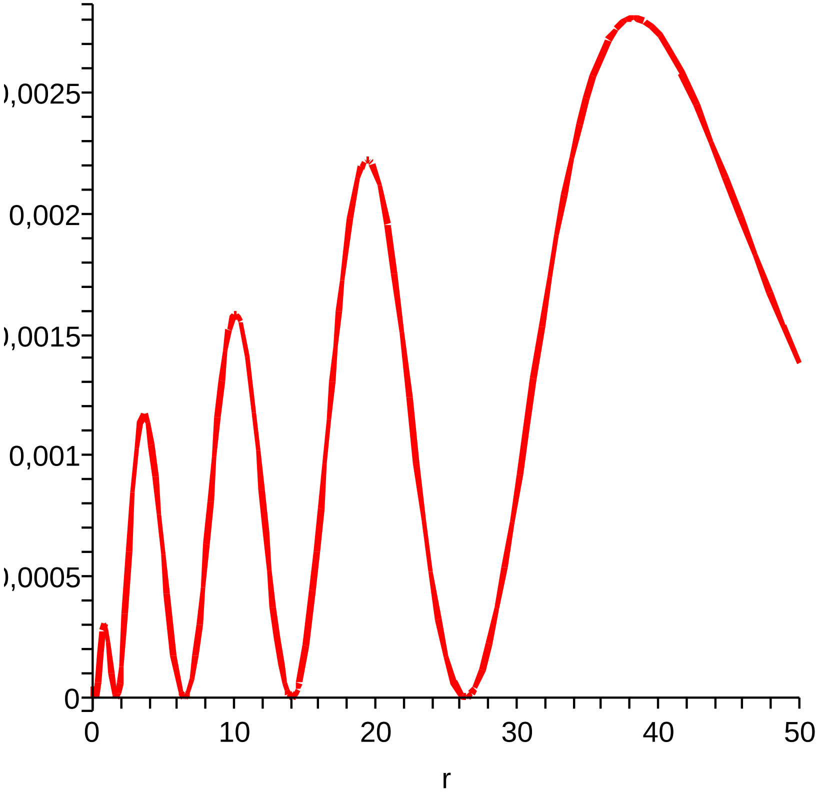
- if one electron is at large distance (“Rydberg electron”):

$$\Psi_N \approx \phi_{ns} \Psi_{N-1}$$

- excitation nodes as in atomic ϕ_{ns} (hydrogen-like!)

Example ^{1}P: ϕ_{6s} radial distribution



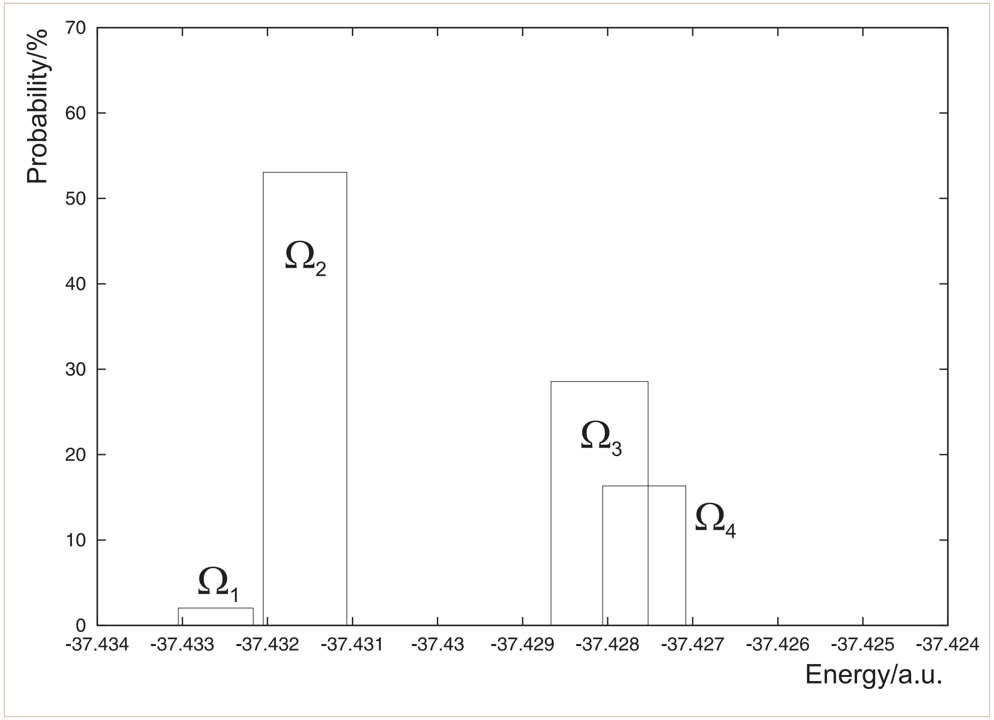


Rydberg states: carbon atom ^{3}P (2p6s) state

nodal domains and energies

Ω_j	$E_0^{(j)}/E_\mathrm{h}$	$\langle r_1 \rangle$
Ω_1	$-37.4332(4)$	1.8
Ω_2	$-37.4315(5)$	41
Ω_3	$-37.4281(6)$	20
Ω_4	$-37.4276(5)$	10
Ω_5	$-36.4630(6)$	15

Relative importance of domains



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2p6s	0.02	−0.136(8)	0.00(1)	0.01

A. Bande, A. Lüchow, F. Della Sala, A. Görling, JCP 124, 114114 (2006).

node optimization for rydberg states

^{1}P (2p6s) Rydberg state: *domain energy optimization*

- method: move 6s nodes (particle in the box), fit orbital to nodes, recalculate domain energies

	E_{orig}	E_{opt}	$\langle r_1 \rangle$
Ω_1	−37.4378(5)	−37.4294(3)	1.5
Ω_2	−37.4311(4)	−37.4310(3)	43
Ω_3	−37.4280(3)	−37.4316(3)	20
Ω_4	−37.4249(4)	−37.4289(3)	10

energies in E_h and distances in bohr, individual standard deviations

- weighted energy and excitation energy (10.89 eV) almost unchanged
- excitation energy remains too high

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carbon monoxide Rydberg states

Carbon monoxide *excitation energies* to Rydberg states with OSLHF/LYP, FN-DMC, and VMC in eV.

State	OSLHF	FN-DMC[a]	VMC[a]	exp.[b]
$^3\Sigma(5\sigma6\sigma)$	10.79	10.48(6)	10.27(5)	10.4
$^1\Sigma(5\sigma6\sigma)$	11.37	10.70(7)	10.70(3)	10.78
$^3\Sigma(5\sigma7\sigma)$	11.65	11.37(7)	11.18(4)	11.3
$^1\Sigma(5\sigma7\sigma)$	11.83	11.47(7)	11.24(4)	11.40

- FN-DMC better than 0.1 eV for a molecule

[a] A. Bande, A. Lüchow, F. Della Sala, A. Görling, JCP 124, 114114 (2006)

[b] E. S. Nielsen, P. Jørgensen, and J.Oddershede, JCP 73, 6238 (1980)

carbon monoxide Rydberg states

Carbon monoxide *singlet-triplet splittings* calculated with OSLHF/LYP, FN-DMC, and VMC in eV.

State	OSLHF	FN-DMC	VMC	exp.
$(5\sigma 6\sigma)$	0.58	0.21(9)	0.43(6)	0.38
$(5\sigma 7\sigma)$	0.18	0.10(9)	0.06(6)	0.10

Fermion sign problem: direct improvement of nodes

current approach:

- take nodal hypersurface from HF or KS Slater determinant (or MCSCF, CIS, PNOCI function) as *fixed node*
- FN-DMC energy is determined by *nodal hypersurface only* (and variational for the ground state)
- *BUT:* nodal hypersurface obtained from *energy minimization* of $\langle\Psi|H|\Psi\rangle = \int \frac{H\Psi}{\Psi}\Psi^2\, d\tau$
- $\Rightarrow$ good energies with inaccurate nodes possible

new idea: Direct optimization of the nodal hypersurface. But how?

- local measure for the accuracy of the nodes

On the nodes of Ψ and Ψ_T

Start: exact wave function Ψ:

$$(H - E)\Psi \;=\; (T + V - E)\,\Psi \;=\; 0$$

- Same nodes for Ψ, $H\Psi$, and $T\Psi$

$$\forall \mathbf{r} : \Psi(\mathbf{r}) = 0 \Rightarrow H\Psi(\mathbf{r}) = T\Psi(\mathbf{r}) = 0$$

But we use: trial wave function Ψ_T and trial energy E_T for DMC:

$$(H - E_T)\Psi_T \;=\; T\Psi_T + (V - E_T)\,\Psi_T \;=\; \chi\,,$$

- χ is small and slowly varying.
- $\Psi_T(\mathbf{r}(\sigma)) \equiv 0$ is nodal hypersurface of Ψ_T. Assume:

$$\tilde{\mathbf{r}}(\sigma) \;=\; \mathbf{r}(\sigma) \;+\; \eta(\sigma)\,\mathbf{n}(\sigma)\,, \qquad (1)$$

- $\tilde{\mathbf{r}}(\sigma)$ is node of $H\Psi_T$ where $\mathbf{n}(\sigma)$ is unit normal vector.
- $\mathbf{n} = \nabla\Psi_T/|\nabla\Psi_T|$ and η is distance between nodal hypersurfaces.

Approximate distance η

First order (multivariate) Taylor series:

$$\Psi_T(\tilde{\mathbf{r}}) = \Psi_T(\mathbf{r} + \eta\ \mathbf{n}) = \Psi_T(\mathbf{r}(\sigma)) + \eta\ \partial_n \Psi_T|_{\mathbf{r}(\sigma)} + O(\eta^2)$$

where $\partial_n \equiv \mathbf{n} \cdot \boldsymbol{\nabla}$. Since $\Psi_T(\mathbf{r}(\sigma)) = 0$:

$$H\Psi_T(\mathbf{r} + \eta\ \mathbf{n}) \ = \ E_T\ \Psi_T(\mathbf{r} + \eta\ \mathbf{n}) + \chi \approx E_T\ \eta\ \ \partial_n \Psi_T|_{\mathbf{r}(\sigma)}\ \ +\ \chi \equiv 0$$

or

$$\eta \approx -\frac{1}{E_T}\ \frac{\chi}{\partial_n \Psi_T}\bigg|_{\mathbf{r}(\sigma)}$$

Now

$$(H - E_T)\Psi_T \ = \ T\Psi_T + (V - E_T)\ \Psi_T \ = \ \chi$$

Thus

$$\eta \approx \ \eta_0 = \frac{1}{2E_T}\,\frac{\boldsymbol{\nabla}^2 \Psi_T}{\partial_n \Psi_T}\bigg|_{\mathbf{r}(\sigma)} \qquad (2)$$

- We now have a simple formula estimating the *local error of the node!*

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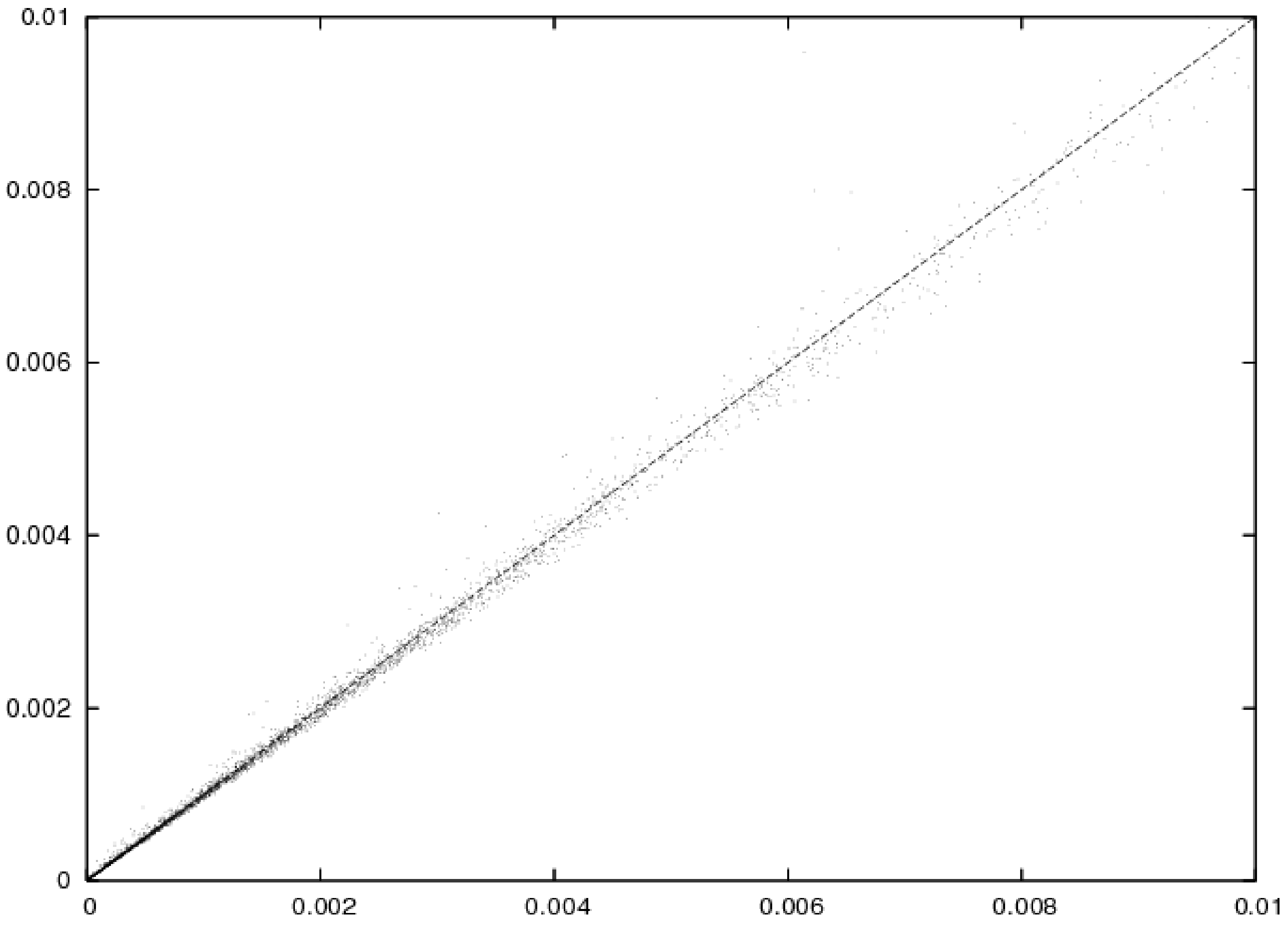
How accurate is distance approximation η_0

- plot of distance η (bisection) vs. approximation η_0 for Be atom wave function (HF with Jastrow)



Fermion sign problem: direct improvement of nodes

New approach:

- *determine quality of nodes locally* (e.g. distance of nodes of $\Psi = 0$ and $H\Psi = 0$, local variance)
- improve nodes by parameter optimization for a sample of points at the nodes (importance sampling)
- most successful so far: estimate for the *distance* of nodal surface of $\Psi = 0$ and $H\Psi = 0$:

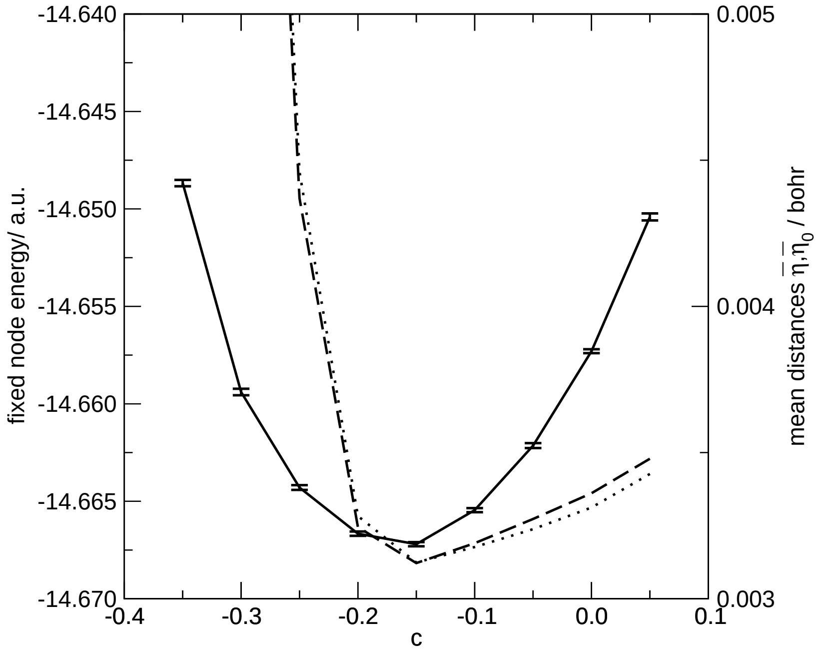
$$\eta_0 = \frac{1}{2E_T} \frac{\nabla^2 \Psi}{\partial_n \Psi}\bigg|_{\mathbf{r}(\sigma)} \tag{3}$$

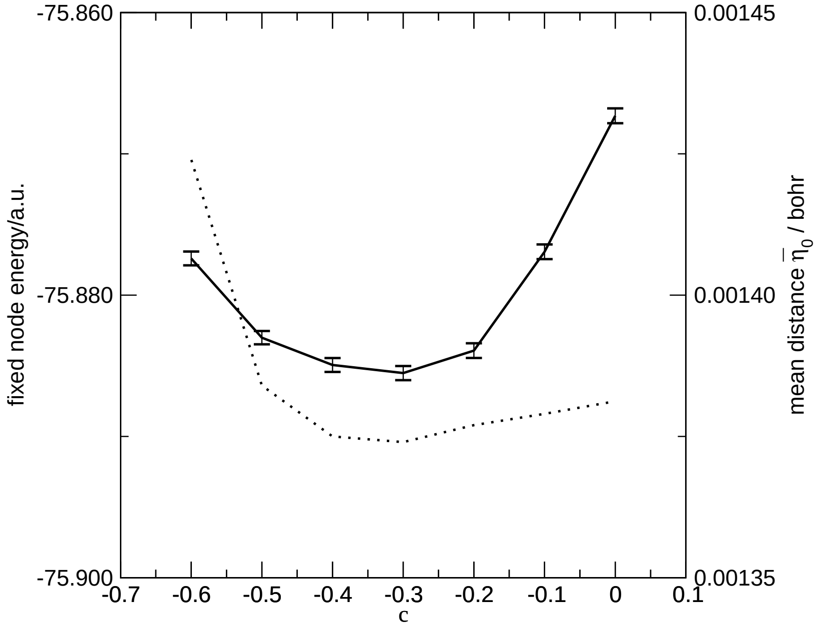
- Minimization of sample mean: very inexpensive

$$\bar{\eta}_0 = \sqrt{\frac{1}{K} \sum_{j=1}^{K} \eta_0(\mathbf{r}_j)^2} \tag{4}$$

- Levenberg-Marquardt-method applicable for many parameters

direct improvement of nodes: first results





- Successfully optimized a 2 CSF wave function for Be atom and C_2 molecule
- In the case of C_2: better nodes than with MCSCF wave function
- *Allows finding “best” nodal hypersurface (lowest node location error) for a given wave function ansatz*

[a] A. Lüchow, R. Petz, T.C. Scott, JCP 126, 144110 (2007)

Other Splittings and Bound

Similarly, get distance ξ between nodal hypersurfaces of Ψ_T and $T\Psi_T$:

$$\frac{1}{2}\frac{\nabla^2\Psi_T}{\xi\partial_n\Psi_T}\bigg|_{\mathbf{r}(\sigma)} \approx E_T - \frac{\partial_n(V\ \Psi_T)}{\partial_n\Psi_T} \quad \text{or} \quad \xi \approx \frac{-T\Psi_T}{(E_T - V)\partial_n\Psi_T - (\partial_n V)\Psi_T} \qquad .$$

- *Establish Newton-Raphson (NR) scheme*

  $$\hat{\mathbf{r}}_{i+1} \ = \ \hat{\mathbf{r}}_i \ + \ e_i \ \mathbf{n},$$

  where $\hat{\mathbf{r}}_0 = \mathbf{r}(\sigma)$ and the error of i^{th} iteration is:

  $$e_i(E,\Psi) \ = \ \frac{-T\Psi(\hat{\mathbf{r}}_i)}{(E-V)\partial_n\Psi(\hat{\mathbf{r}}_i) \ - \ (\partial_n V)\Psi(\hat{\mathbf{r}}_i)} \tag{5}$$

- *Self-Consistent NR scheme*: $e_i(E_T,\Psi_T)$ where Ψ_T is *updated* with the improved nodes at each iteration i.e. $\Psi_T(\mathbf{r};\hat{\mathbf{r}}_{i+1}) \leftarrow \Psi_T(\mathbf{r};\hat{\mathbf{r}}_i)$.
- Iteration requires fitting of trial wave function to new nodes.

Self-consistent Newton-Raphson scheme

Error $|e_i|$ of Self-Consistent Newton-Raphson scheme (SCNR) in bohr:

i	Hydrogen 3s state[a]		Hooke's Atom[b]	He $2\,^3S(1s2s)$[c]
0	0.660851e-1	0.3192854	0.13614731	0.8242796e-2
5	0.161150e-2	0.3838903e-2	0.5172530e-3	0.5349413e-2
10	0.609075e-4	0.1431900e-3	0.2130606e-5	0.3480515e-2
15	0.228432e-5	0.5369231e-5	0.8778382e-8	0.2267004e-2
20	0.856610e-7	0.2013420e-6	0.3616815e-10	0.1477277e-2

[a] Trial nodes $1.93833\ldots, 6.63309\ldots \rightarrow$ True nodes $\frac{3}{2}(3 \pm \sqrt{3})$

[b] Trial node at $r_{12} = -2.2 \rightarrow$ True node $r_{12} = -2$.

[c] Trial node at $s = 1.0$, $u = 0.5$, $t = -0.1 \rightarrow$ True node $t = 0$.

[a] T.C. Scott, A. Lüchow, J. Phys. B, 40, 851 (2007)

Vanadium Oxides with Quantum Monte Carlo

transition metal compounds are often difficult for computational chemistry

- strong non-dynamical correlation due to excitations within d shell
- many electronic states close to ground state
- strong dynamical correlation
- relativistic contributions

standard ab initio techniques:

- HF fails to describe non-dynamical correlation
- MP2 often very inaccurate
- Coupled cluster techniques often fairly accurate (but expensive)
- DFT often surprisingly good
- multireference method with dynamical correlation desired
  - MRCI, CASPT2

Vanadium Oxides with Quantum Monte Carlo

why QMC?

- dynamical correlation with Jastrow correlation factor
- non-dynamical correlation with multi-determinant guide functions
  - but: large numbers of determinants expensive
- relativistic effects with (localized) scalar relativistic pseudo potential
- good scaling behaviour compared to coupled cluster or MRCI methods

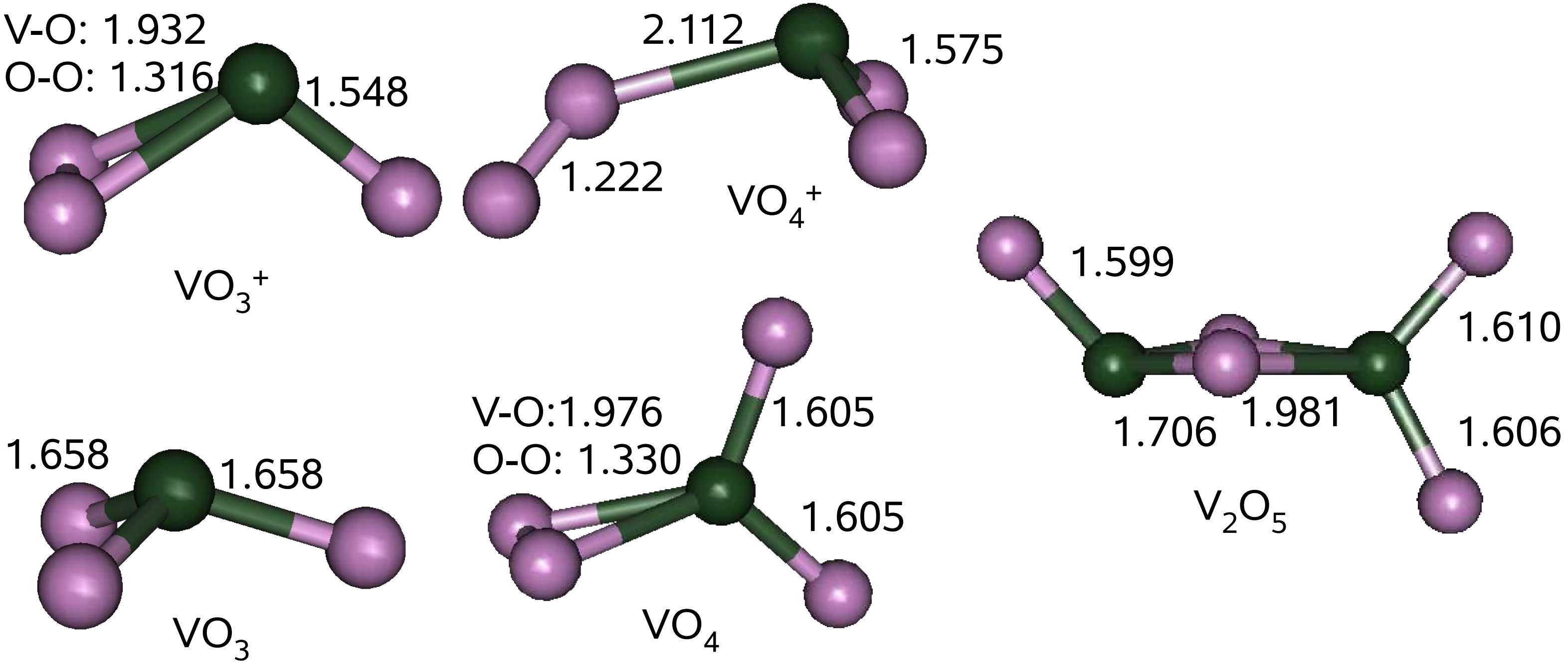
Vanadium Oxides with Quantum Monte Carlo

this investigation:

- VO,VO_2,VO_3,VO_4,V_2O_5 and its cations as examples
- How accurate is QMC with *single* determinant?
- Which orbitals are best for guide function?
  - Can KS orbitals catch non-dynamical correlation for DMC?
- Stuttgart scalar relativistic PP for V
- new Burkatzki/Dolg QMC-PP for O

Vanadium Oxides with Quantum Monte Carlo

BP86/TZVP optimized geometries. Bond lengths are given in Å.



Vanadium Oxides with Quantum Monte Carlo

Atomization energies in eV for VO and VO_2:

	VO	VO_2
Expt	6.51(20)	12.37
DMC/BP86	6.51(1)	11.83(2)
DMC/B3LYP	6.26(1)	11.58(2)
B3LYP	6.53	11.97
CCSD(T)	6.21	10.88

- better accuracy with BP86 than B3LYP nodes
- single reference DMC more accurate than CCSD(T)

Vanadium Oxides with Quantum Monte Carlo

Oxygen abstraction energies in eV: $VO_2^{(+)} \longrightarrow V^{(+)}O + O$

	VO_2	VO_2^+
Expt	5.83(28)	3.60(36)
DMC/BP86	5.32(2)	3.90(1)
B3LYP	5.45	4.03
CCSD(T)	4.67	4.24

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Vanadium Oxides with Quantum Monte Carlo

trends for oxygen abstraction energies in eV

	DMC/BP86	B3LYP
$VO_2 \rightarrow VO+O$	5.32(2)	5.45
$VO_3 \rightarrow VO_2+O$	3.60(2)	4.04
$VO_4 \rightarrow VO_3+O$	3.97(3)	3.97
$V_2O_5 \rightarrow VO_3+VO_2$	6.09(4)	5.40

Vanadium Oxides with Quantum Monte Carlo

vertical and adiabatic ionization potential in eV

	VO (v)	VO (a)
Expt	7.31(1)	7.2386(4)
DMC/BP86	7.24(1)	7.17(1)
B3LYP	7.42	7.37
CCSD(T)	7.03	7.00

Conclusions

conclusions:

- FN-DMC for excited states possible. But: careful if domain energies differ
- solution: average over (many) DMC runs starting from individual walkers of VMC sample
- excitation energies with accuracy of 0.1 eV possible for Rydberg states
- direct optimization of nodes can be done by minimizing distance of nodes of Ψ_T and $H\Psi_T$ for model problems.
- direct node optimization successful for few atoms and molecules
- good accuracy for vanadium oxides with only one determinant obtained: at least as good as CCSD(T)
- higher accuracy of few systems would require multireference DMC

Acknowledgements

- Annika Bande, RWTH Aachen university
- Tony Scott, RWTH Aachen university
- Christian Dietrich, Münster university

Collaborations:

- Stefan Grimme, Münster
- Andreas Görling, Erlangen
- Fabio Della Sala, Lecce, Italy
- Reinhold Fink, Würzburg

Financial support:

- from Deutsche Forschungsgemeinschaft (DFG)

DMC: Computational Details and Effort

Algorithm (part):

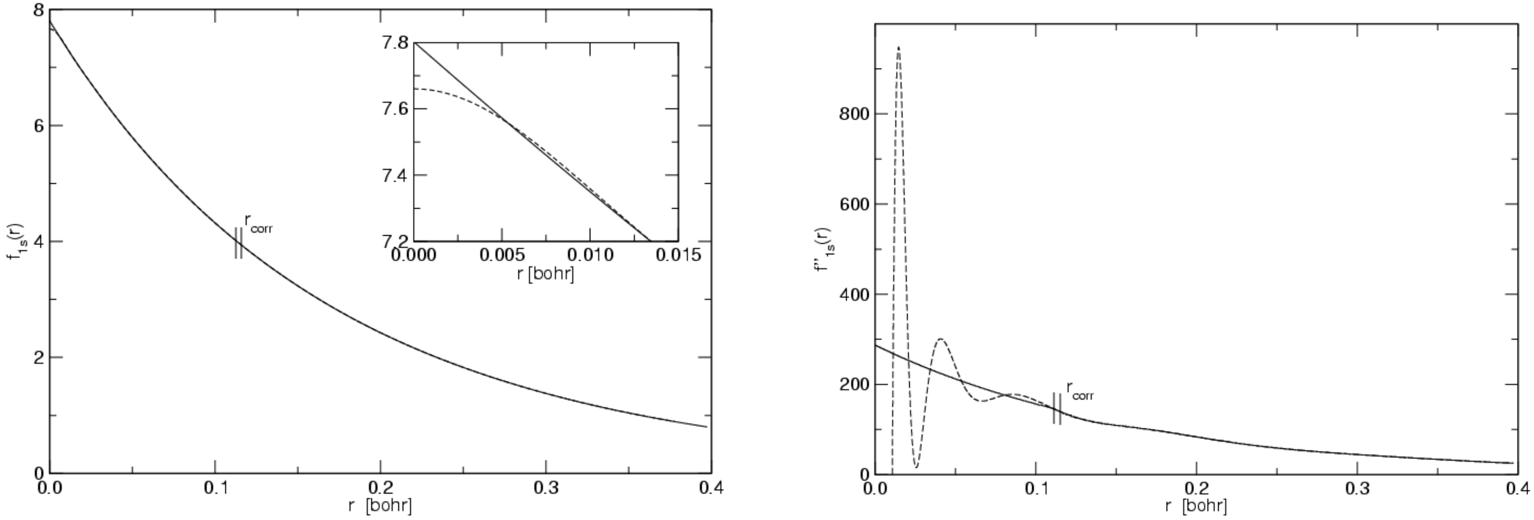
- calculate AOs at current electron position
  (cubic splines, cusp correction)
- calculate MOs from AOs
  or: direct 3d-interpolation for MOs
- calculate $\Phi_{\mathrm{det}}(\mathbf{r})$ as (sum of) determinant(s)
  using LU decomposition
- also: $\nabla\Phi_{\mathrm{det}}(\mathbf{r}), \nabla^2\Phi_{\mathrm{det}}(\mathbf{r})$
  updating algorithm
- same for $e^U, \nabla e^U, \nabla^2 e^U$
- calculate $E_L(\mathbf{r}) = -\dfrac{\nabla^2\Phi_G(\mathbf{r})}{2\Phi_G(\mathbf{r})} + V(\mathbf{r})$

QMC: cusp correction for standard basis functions

- GTOs have no cusp at nucleus → fluctuating local energy near nucleus
- contracted GTO basis sets do not work for QMC (without pseudo potentials) → use STO basis
- standard contracted GTO basis sets can be used after *cusp correction*:
  – exponential near nucleus, interpolating polynomial, rest unchanged
  – corrected basis function replaced by cubic splines

QMC: cusp correction for standard basis functions

cusp correction for carbon 1s cc-pVTZ basis function and its 2nd derivative:

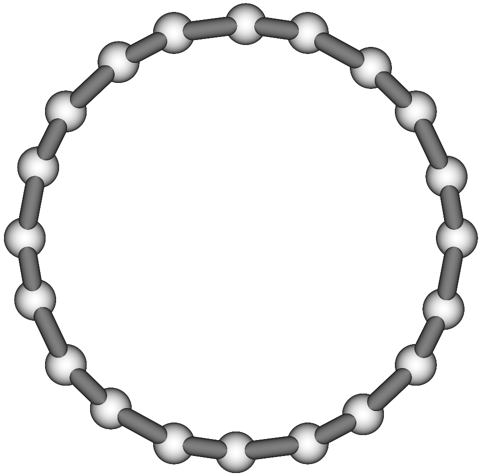


- using standard all-electron ab initio wavefunctions with QMC
- or ECPs, but: only localized ECPs possible, localization $W_{loc} = \frac{W\Phi_G}{\Phi_G}$

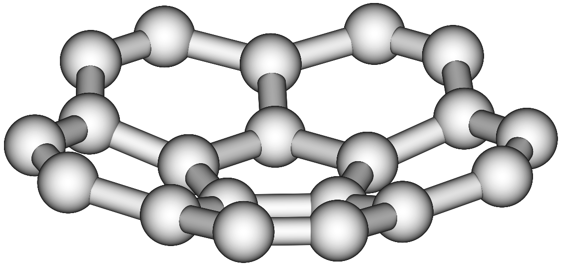
S. Manten and A. Lüchow, JCP 115, 5362 (2001)

FN-DMC: carbon clusters

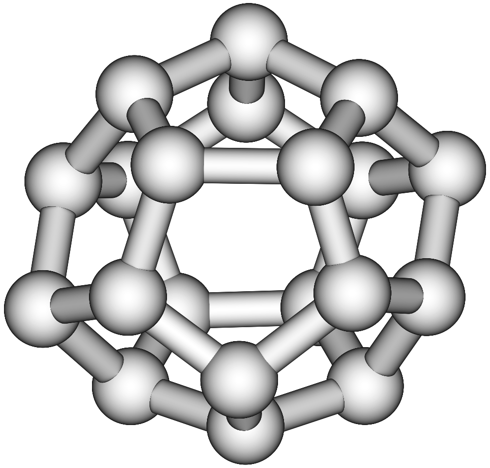
DMC/HF calculations for carbon clusters C_{20}



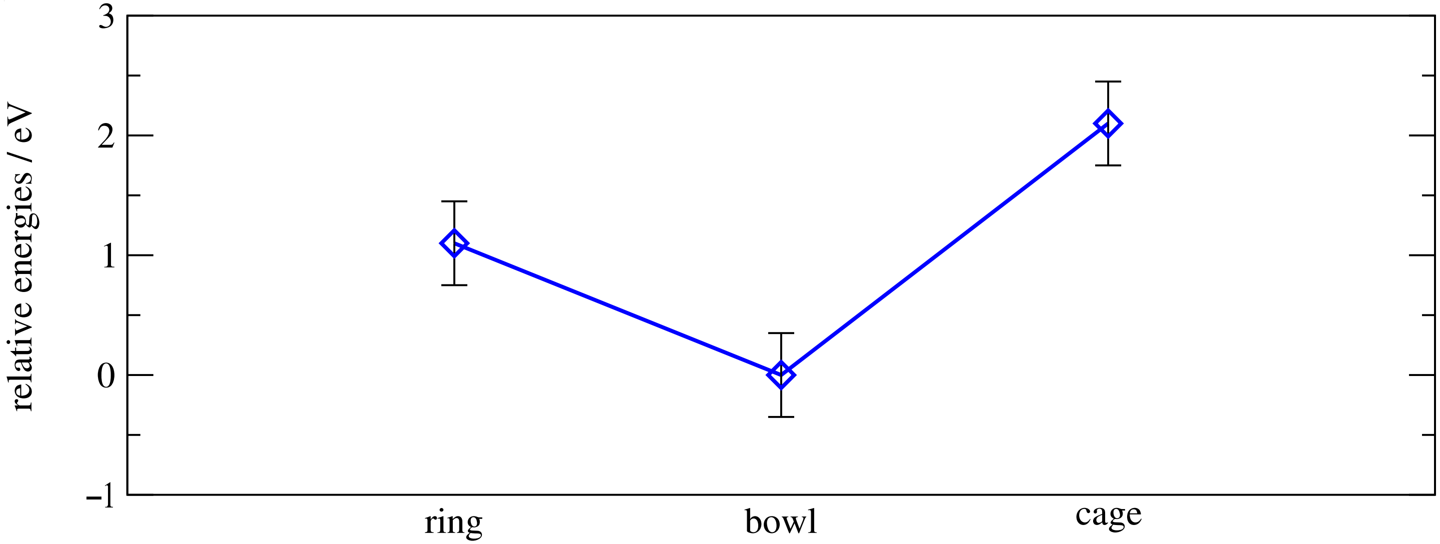
ring



bowl



cage



S. Sokolova, A. Lüchow, J. B. Anderson, Chem. Phys. Lett. 323, 299 (2000)

nodal regions for C atom

- ^{3}P ground state: *regional energies* and topological characterization

		spin up				spin down	
	$E_{\text{FN-DMC}}$	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle r_3 \rangle$	$\langle r_4 \rangle$	$\langle r_5 \rangle$	$\langle r_6 \rangle$
Ω_1	−37.830	1.4±1.0	1.4±1.0	1.4±1.0	1.4±1.0	1.6±0.7	0.3±0
Ω_2	−37.416	47±5	1.2±1.0	1.2±1.0	1.2±1.0	1.6±0.7	0.3±0
Ω_3	−37.137	1.3±1.0	1.3±1.0	1.3±1.0	1.3±1.0	24±2	0.3±0
Ω_4	−34.840	44±7	43±7	26±4	0.3±0.1	1.4±0.6	0.3±0
Ω_5	−26.320	1.1±0.8	1.1±0.8	1.1±0.8	1.1±0.8	24±2	2.2±0

energies in E_h and distances in bohr, individual standard deviations

- spurious nodes at very large distances
- no influence when starting with Ψ_T^2 VMC sample