



... for a brighter future

CASSCF Calculations Via Variational Two-Electron Reduced-Density-Matrix Theory

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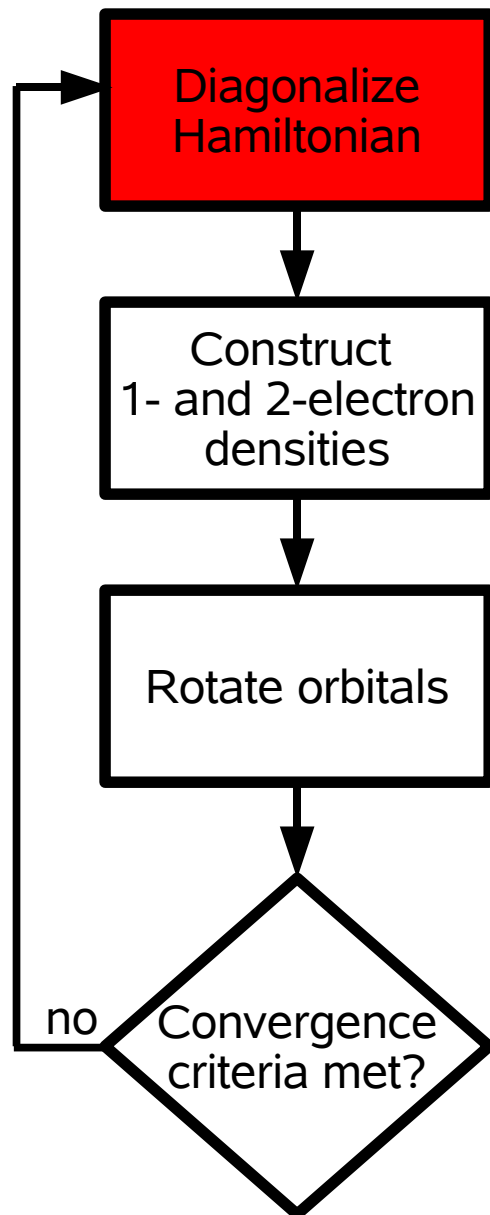
Outline

- CASSCF
 - *why do we need it?*
 - *outline of 2-step procedure*
- Variational 2-RDM theory
 - *N-representability and positivity conditions*
- Orbital rotations
- Applications
 - Potential energy curves for small diatomics
 - n-Acene series and diradical character

CASSCF

- Hartree-Fock theory yields qualitatively correct results for most molecules near equilibrium
- In many cases, however, one has to include multiple configurations at the zeroth order
 - bond breaking (N_2)
 - HCH angle bend in methylene
- Need to optimize both the orbitals and the CI coefficients

2-Step CASSCF



- Orbitals and CI coefficients sequentially optimized at each iteration
- Diagonalization is the computational bottleneck

$$\dim_H \approx \binom{r_{act}}{n_{act}}^2$$

- Is there a way to eliminate unfavorable scaling of the diagonalization step?

Energy expression in terms of the 2-RDM

- Electrons are indistinguishable
- Hamiltonian contains two-electron interactions

$$E = \text{Tr}[^2K \ ^2D]$$
$$^2K_{k,l}^{i,j} = \frac{1}{N-1}(\delta_{i,k}h_{j,l} + \delta_{j,l}h_{i,k}) + (ik|jl)$$
$$^2D_{k,l}^{i,j} = \langle \psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | \psi \rangle$$

- Cannot simply compute energy by varying elements of the 2-RDM
- Need conditions to ensure that 2-RDM corresponds to an N -electron wave function ^a

^a A. J. Coleman, *Rev. Mod. Phys.*, **35** 668 (1963)

N-representability and positivity

- Hierarchy of conditions can be derived by considering basis functions $\hat{C}_i|\psi\rangle = |\phi_i\rangle$ whose overlap is nonnegative

$$M_j^i = \langle \phi_i | \phi_j \rangle \geq 0$$

- $\{\hat{a}_i, \hat{a}_i^\dagger\}$ generates the 1-electron and 1-hole RDMs

$${}^1D_j^i = \langle \psi | \hat{a}_i^\dagger \hat{a}_j | \psi \rangle \quad {}^1Q_j^i = \langle \psi | \hat{a}_i \hat{a}_j^\dagger | \psi \rangle$$

- $\{\hat{a}_i \hat{a}_j, \hat{a}_i^\dagger \hat{a}_j^\dagger, \hat{a}_i^\dagger \hat{a}_j\}$ generates the 2-electron, 2-hole and electron-hole RDMs

$${}^2D_{k,l}^{i,j} = \langle \psi | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k | \psi \rangle \quad {}^2Q_{k,l}^{i,j} = \langle \psi | \hat{a}_i \hat{a}_j \hat{a}_l^\dagger \hat{a}_k^\dagger | \psi \rangle \quad {}^2G_{k,l}^{i,j} = \langle \psi | \hat{a}_i^\dagger \hat{a}_j \hat{a}_l^\dagger \hat{a}_k | \psi \rangle$$

- Basis function linearly independent \rightarrow density matrices are not

Variational Optimization of Energy

- The positivity constraints on the RDMs and the linear mappings between them define a semi-definite program

$$E = \min(C \bullet X) \quad \begin{cases} A \bullet X = b \\ X \geq 0 \end{cases}$$

- Second-order methods are expensive
- Scaling may be reduced by matrix factorization^{a,b}

$$L(R, y, \sigma) = C \bullet RR^T - \sum_{i=1}^m y_i [C_i(R)] + \sigma/2 \sum_{i=1}^m [C_i(R)]^2$$

- Memory (r^4); floating-point operations (r^6)

^a M. Burer and R. D. C. Monteiro, *Math. Prog.*, **95** 329 (2003)

^b D. A. Mazziotti, *Phys. Rev. Lett.*, **93** 213001 (2004)

Jacobi rotations

- For given 1- and 2-electron densities we wish to determine the transformation \mathbf{T}

$$\bar{\phi}_i = \sum_j T_{ji} \phi_j$$

that minimizes the energy

- Express overall transformation as a sequence of Jacobi rotations between orbital pairs $(\mathbf{J}_{ij})^a$
- Energy is invariant to mixing between orbitals in the core and active spaces

$$\mathbf{T} = \left(\prod_{i=1}^{r_c} \prod_{j=r_c+1}^{r_T} \mathbf{J}_{ij} \right) \left(\prod_{i=r_c+1}^{r_c+r_a} \prod_{j=i+1}^{r_T} \mathbf{J}_{ij} \right)$$

^a F. D. Murnaghan, *The Unitary Group and Rotation Groups* (Spartan Books, Washington, 1962)

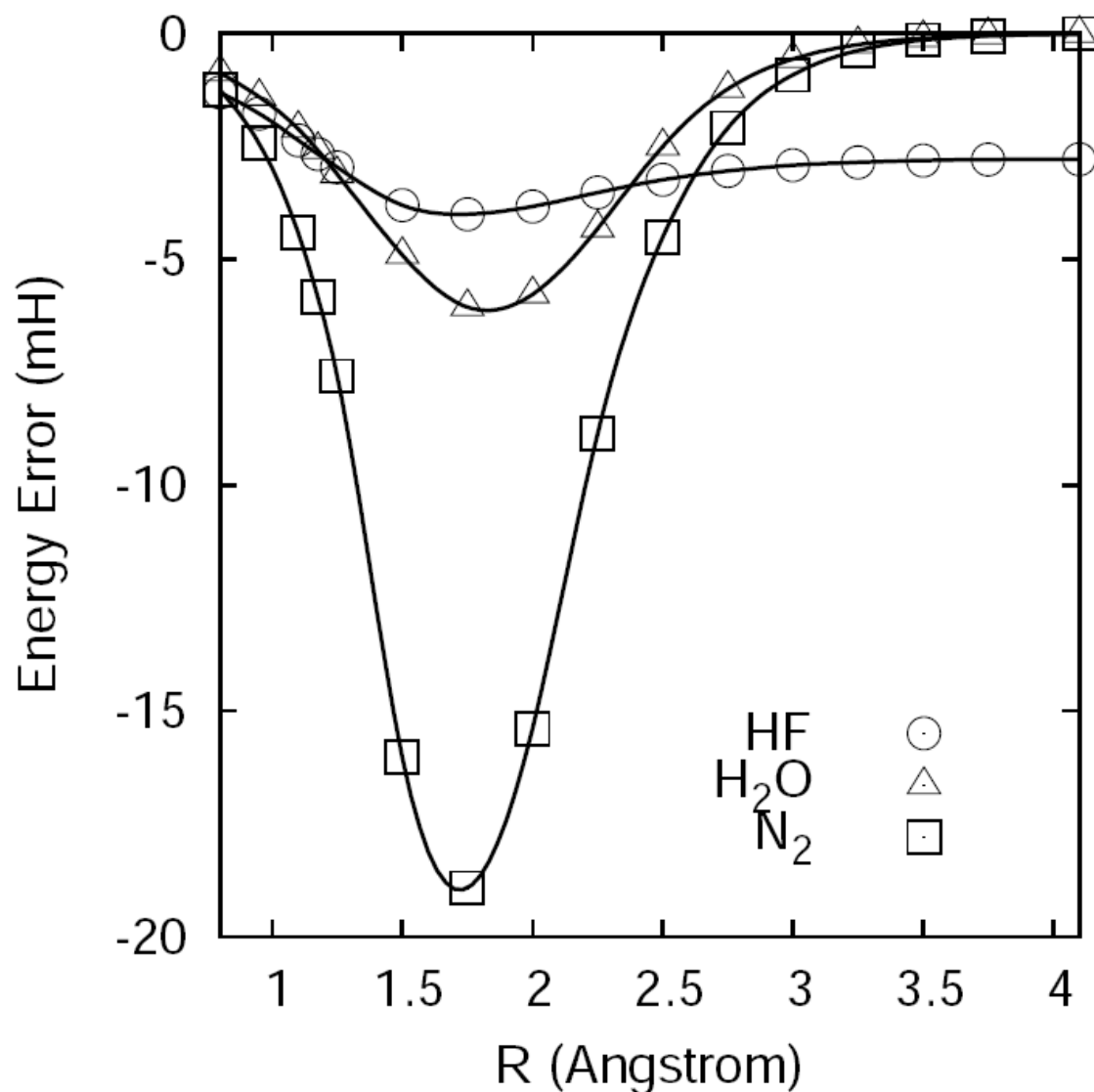
Jacobi rotations ...

- While one such transformation is guaranteed to lower the energy, it is unlikely to have minimized the energy
- Need to perform several (5-10) sweeps over orbital pairs
- Explicit formulas for updated 1- and 2-electron integrals have been derived ^a
- This approach has been shown to yield identical results to those from other methods implemented in GAMESS ^b

^a J. Ivanic and K. Ruedenberg, *J. Comput. Chem.*, **24** 1250 (2003)

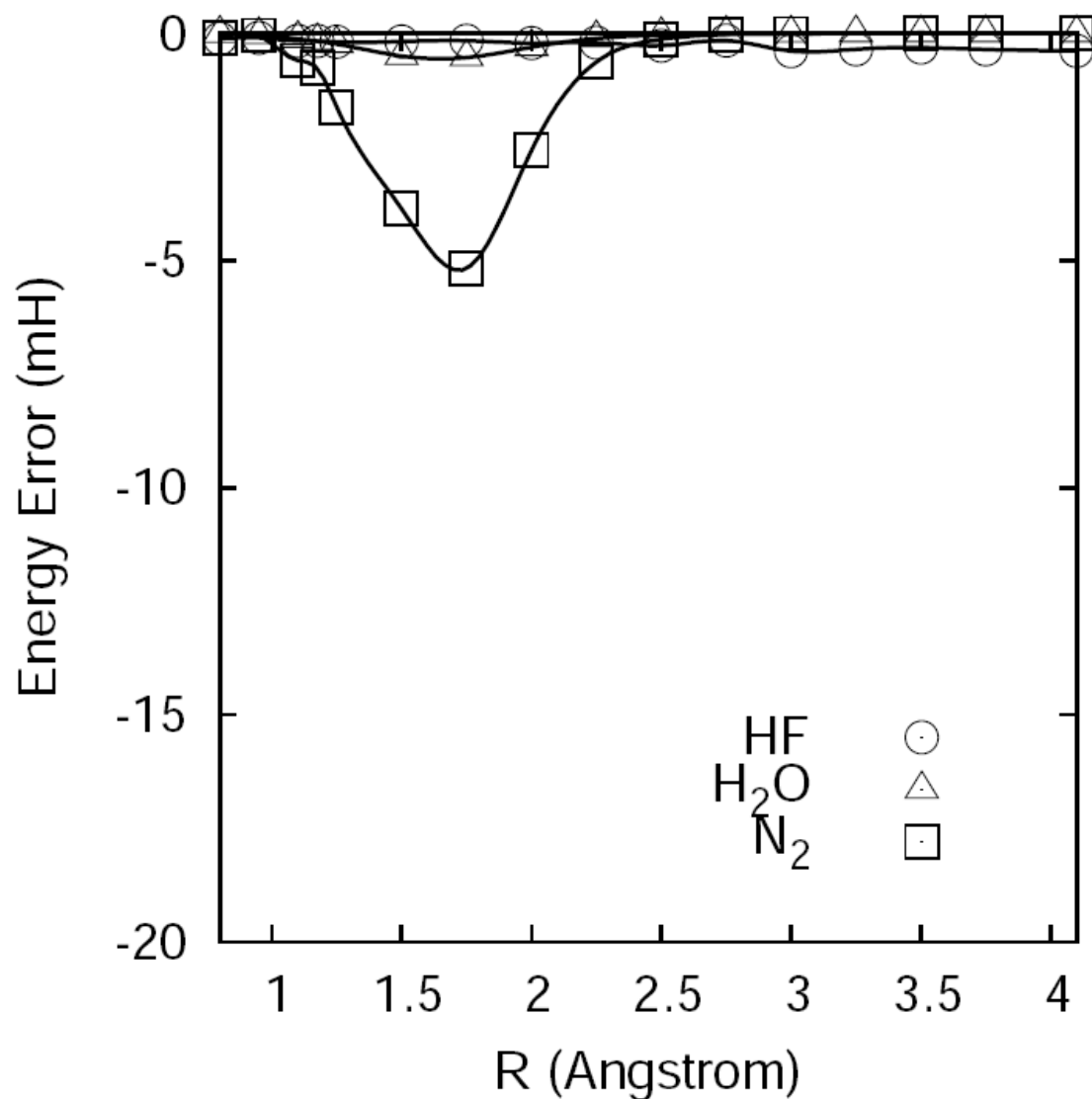
^b M. W. Schmidt, K. K. Baldridge, J. A. Boatz *et al.*, *J. Comput. Chem.* **14**, 12347 (1993)

Accuracy of Two-positivity Conditions



- 2-positivity yields useful accuracy
- Most difficulty in the spin-recoupling region

Improving Accuracy Partial Three-positivity Conditions



- PES for HF and water very accurate
NPE < 1mH
- Error in the PES for N₂ is significantly reduced

Accuracy of 2-positivity and basis sets

Molecule	Nonparallelity Errors (mH)			
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
HF	2.7	2.9	3.1	3.2
H ₂ O	6.1	6.1	6.1	6.1
N ₂	18.9	18.8	18.9	18.9

- NPE does not significantly depend on the basis set size
- Absolute errors are also similar in all basis sets

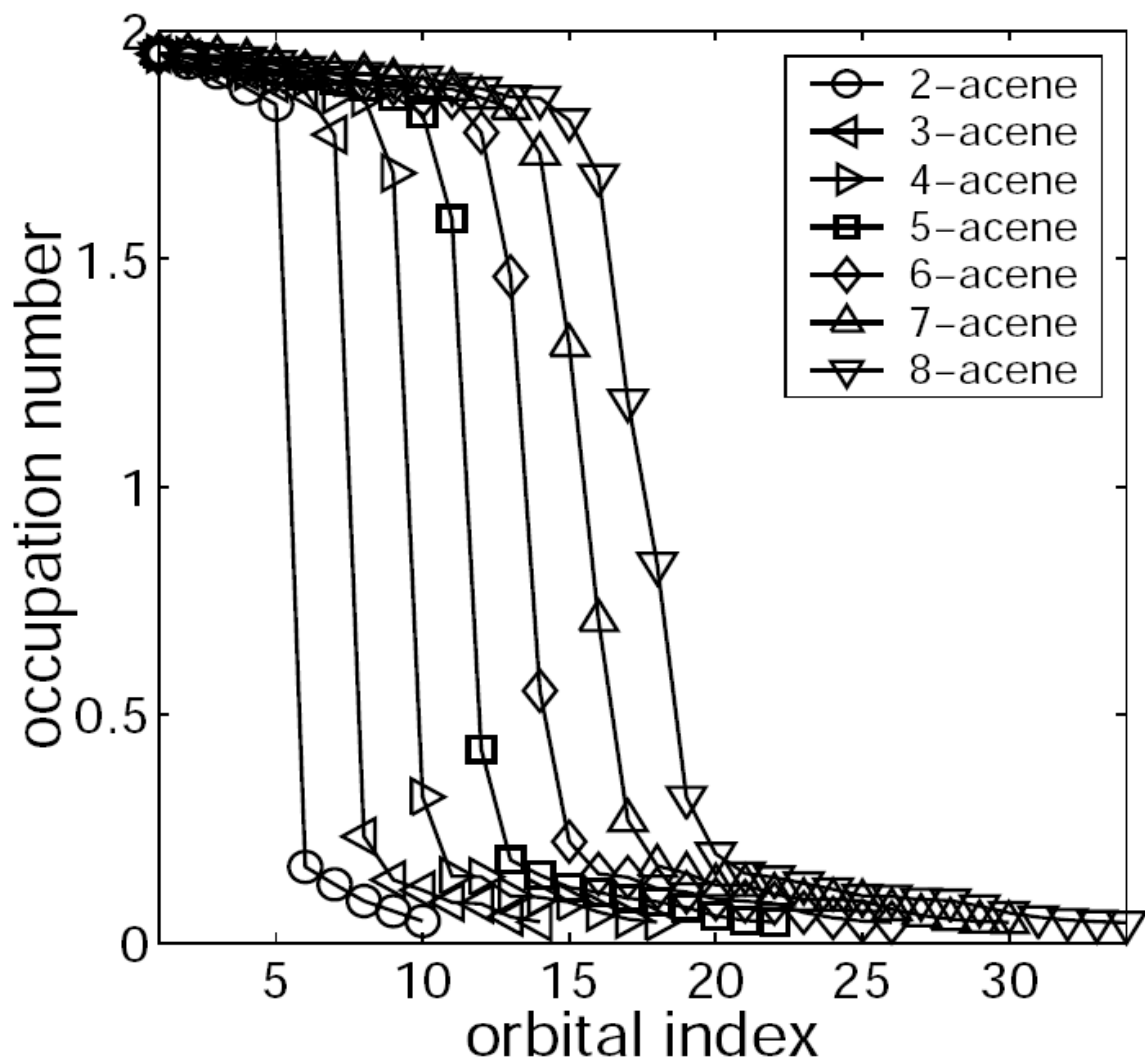
The Greater Challenge ... Acene Series

	$[n_{act}, r_{act}]$	N_{2POS}	N_{CSF}
2-Acene	[10,10]	75256	4936
3-Acene	[14,14]	28862	69116
4-Acene	[18,18]	78814	112298248
5-Acene	[22,22]	175814	19870984112
6-Acene	[26,26]	342902	3725330089248
7-Acene	[30,30]	607726	728422684135920
8-Acene	[34,34]	1002542	147068001734374624

- 5- and higher acenes out of reach of traditional CASSCF methods
- Ground state is known to be singlet ^a
- Closed-shell or singlet-coupled diradicals?

^a J. Hachmann, J. J. Dorando, M. Alivés, and G. K.-L. Chan,
J. Chem. Phys., **127** 134309 (2007)

Occupation Numbers for the Acene Series



- Clearly not closed shell
- Occupation numbers of HONO and LUNO orbitals approach unity for larger acenes

Conclusions

- Variational RDM theory affords the treatment of active spaces that are too large for traditional CASSCF methods
- 2-positivity conditions yield useful accuracy
- NPE insensitive to basis set size
- Accuracy can be improved by imposing full or partial 3-positivity conditions
- Applications to other PAHs in progress

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