

## RG methods for Quantum Chemistry

Numerical Treatment of SC systems: Where are we?

- Powerful numerical techniques, but:
  - Sensitive models, complicated phase diagrams
  - Uncertain models: additional terms can have a big effect. Making models an art.

Therefore: we need to develop methods that connect more directly to *ab initio* calculations.

- “LDA + U” models solved by DMFT or other methods a step in the right direction.
- RG should be the basis for an ideal method.

The approach I’ve been taking:

1. DMRG for *ab initio* quantum chemistry on small molecules
  - Work up to strongly correlated systems, check model calcs.
  - Improve quantum chemistry.
2. Numerical canonical transformations of second quantized Hamiltonians to create an RG that can derive models.

## Quantum Chemistry–Standard Approach

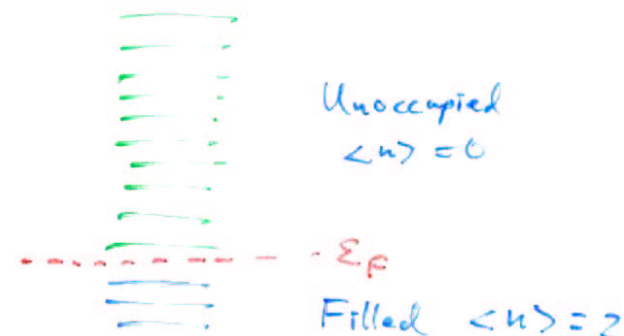
Basis Set: Gaussians × spherical Harmonics, centered on nuclei. Several Gaussians are combined to form one basis function. (Integrals easy with Gaussians.)

Overlap Matrix:  $O_{ij} = \langle \phi_i | \phi_j \rangle$

Hartree Fock (SCF): Determinantal wavefunction. Get uncorrelated energy, orthogonal HF orbitals

$$\psi_i = \sum_j a_{ij} \phi_j$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$



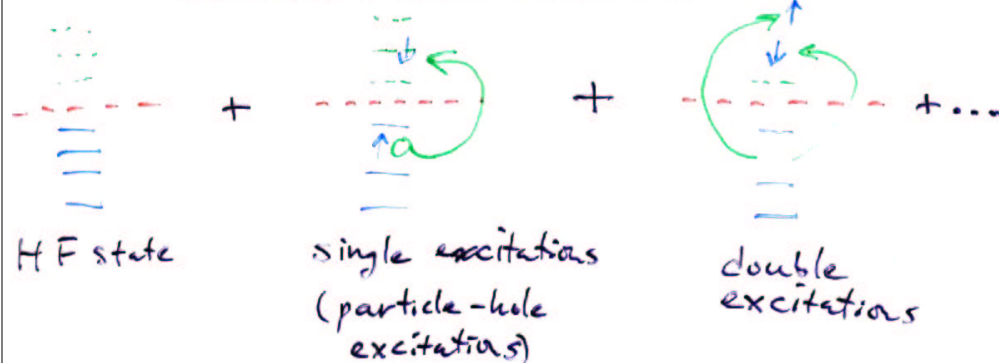
Hamiltonian in HF basis:

$$H = \sum_{ij\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijkl} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}$$

Correlations: Various methods, usually start with HF orbitals.

Configuration Interaction:

- 1) Form subspace of total Hilbert space, as a limited set of determinants in HF basis.



Typically singles through quadruples are used on "hard" systems.

- 2) Diagonalize exactly within subspace.
- 3) Justification: perturbation theory.

Multireference CI:

Do excitations relative to several reference states.

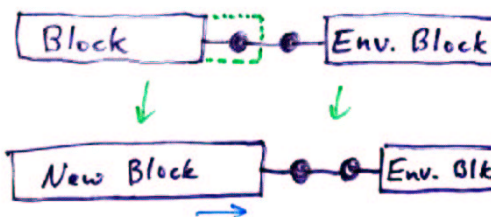
Others: Perturbation theory, coupled cluster methods, etc.

Numerical Simulations-DMRG

Numerical RG's (Wilson '74): Solve the system a little bit at a time. Represent system by a set of block Hamiltonian eigenstates. Only works well for impurity problems.

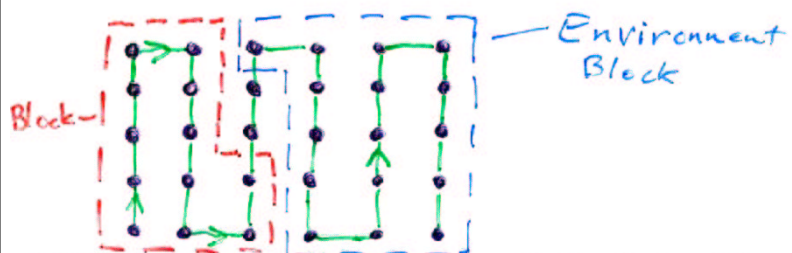
Density Matrix Renormalization Group (White '92): Represents system by a set of many-body states, derived from a density matrix. Includes environment block, and includes sweeps back and forth through lattice.

Works extremely well for 1D problems (1+1 D). Accuracy often increases exponentially with number of states kept  $m$ !



Sweep =  
left-to-right,  
then  
right-to-left

Two dimensions: map onto 1D



DMRG loses accuracy exponentially fast with width! However, still feasible up to about  $L \times 8$ .

Need # of states kept  $m$  large, many sweeps!



## DMRG for Quantum Chemistry

Basic Approach: Each <sup>(HF)</sup>orbital is treated as a “site” in a lattice. The Hamiltonian is long-ranged and complicated. Orbitals can be ordered in order to

- minimize strength of longer-ranged interactions, or
- in order of Hartree Fock orbital energies.

First Problem: There are  $N^4$  terms in the Hamiltonian, so naively need to keep  $(N^4)N$   $m \times m$  matrices.

→ Sum together all terms  $V_{ijkl}c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}$  into one  $H_{\text{block}}$  matrix once sites  $ijkl$  are all in the block (always done in DMRG). Now have only  $\sim N^3$  matrices/block

Further Improvement: There are  $\sim N^3$  matrices per block made out of 3-operator terms. To reduce them, construct complementary operators like

$$O_{i\sigma} = \sum_{jkl\sigma'} V_{ijkl} c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma}$$

Now  $H$  has terms like

$$\sum_{i\sigma} c_{i\sigma}^\dagger O_{i\sigma}.$$

This reduces  $\sim N^3$  matrices per block down to  $\sim N$ .

Now the dominant part of a block is  $\sim N^2$  operators of the form  $c_{k\sigma'} c_{l\sigma}$  or  $c_{j\sigma'}^\dagger c_{k\sigma'}$ , etc. This is reasonable for storage, but the calculation time is still  $(N^4 m^3)N$ :

$$H = \sum_{ij \in L} \sum_{kl \in R} V_{ijkl} [c_i^\dagger c_j^\dagger] [c_k c_l] + \dots$$

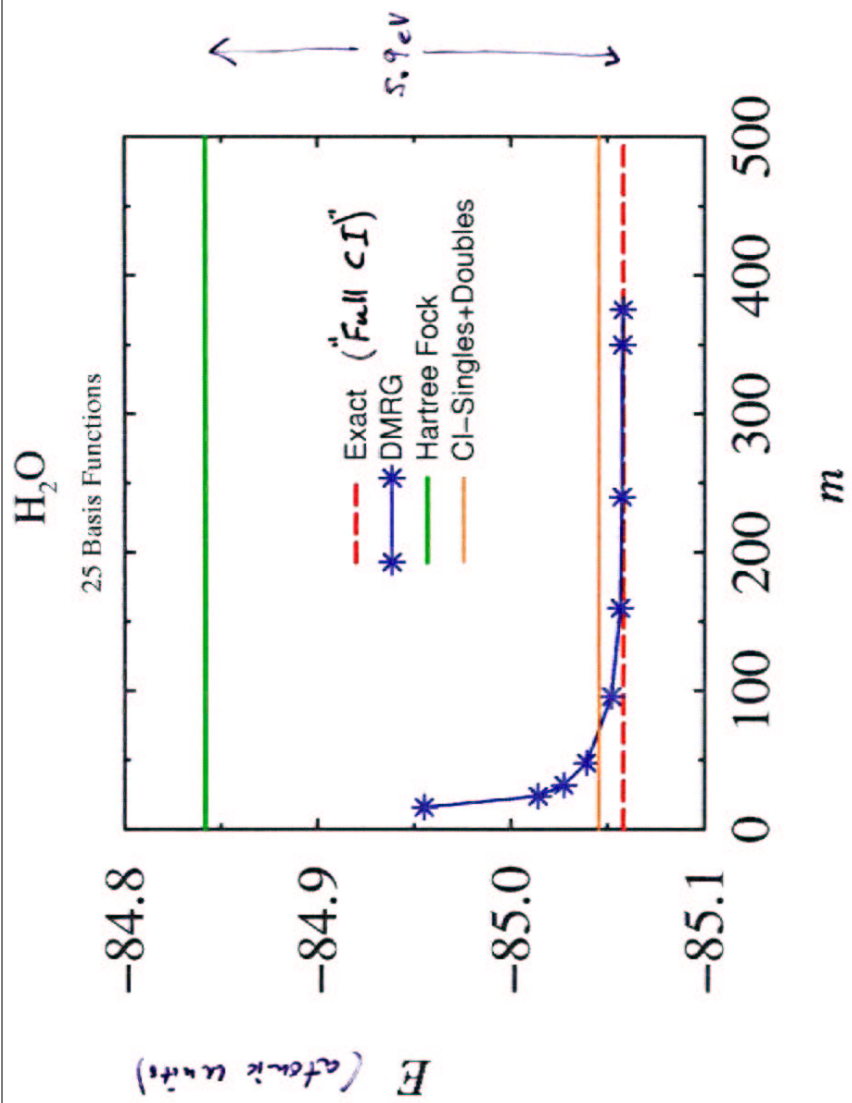
Solution: Construct more complementary operators like

$$O_{ij}^R = \sum_{kl \in R} V_{ijkl} [c_k c_l] \quad \forall ij \in L$$

Then there are  $\sim N^2$  operators in

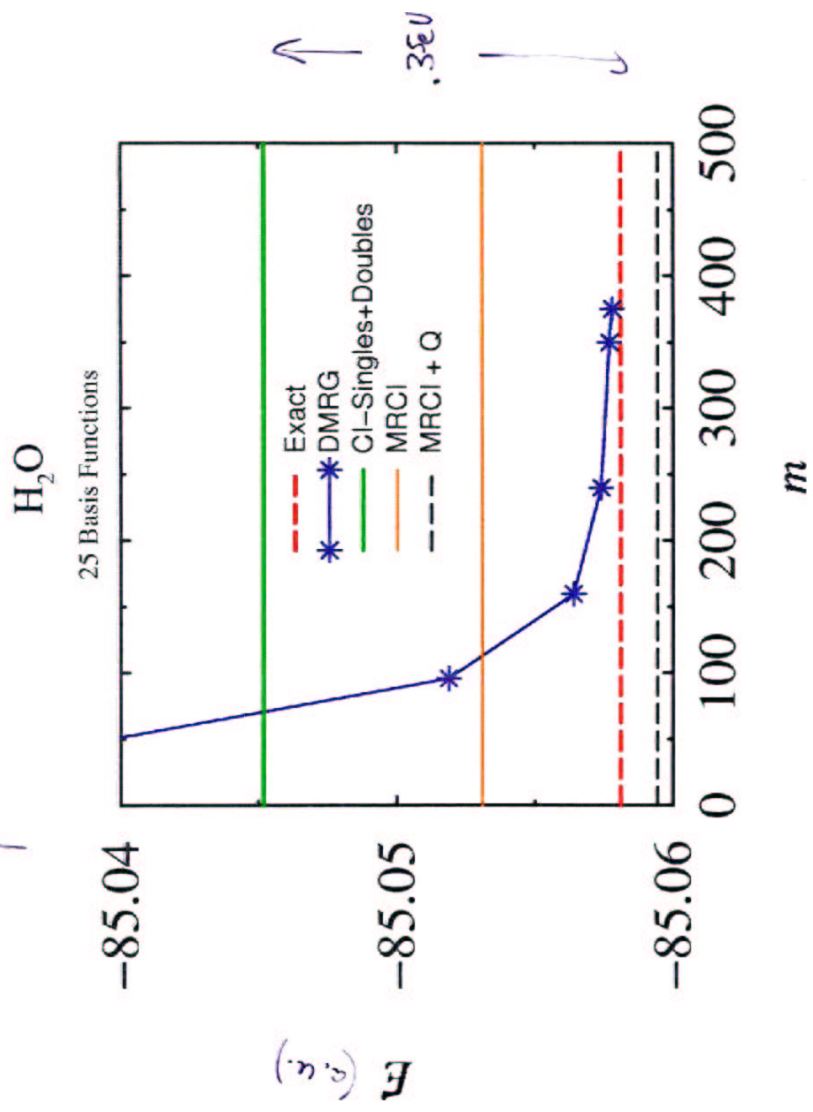
$$H = \sum_{ij \in L} [c_i^\dagger c_j^\dagger] [O_{ij}^R] + \dots$$

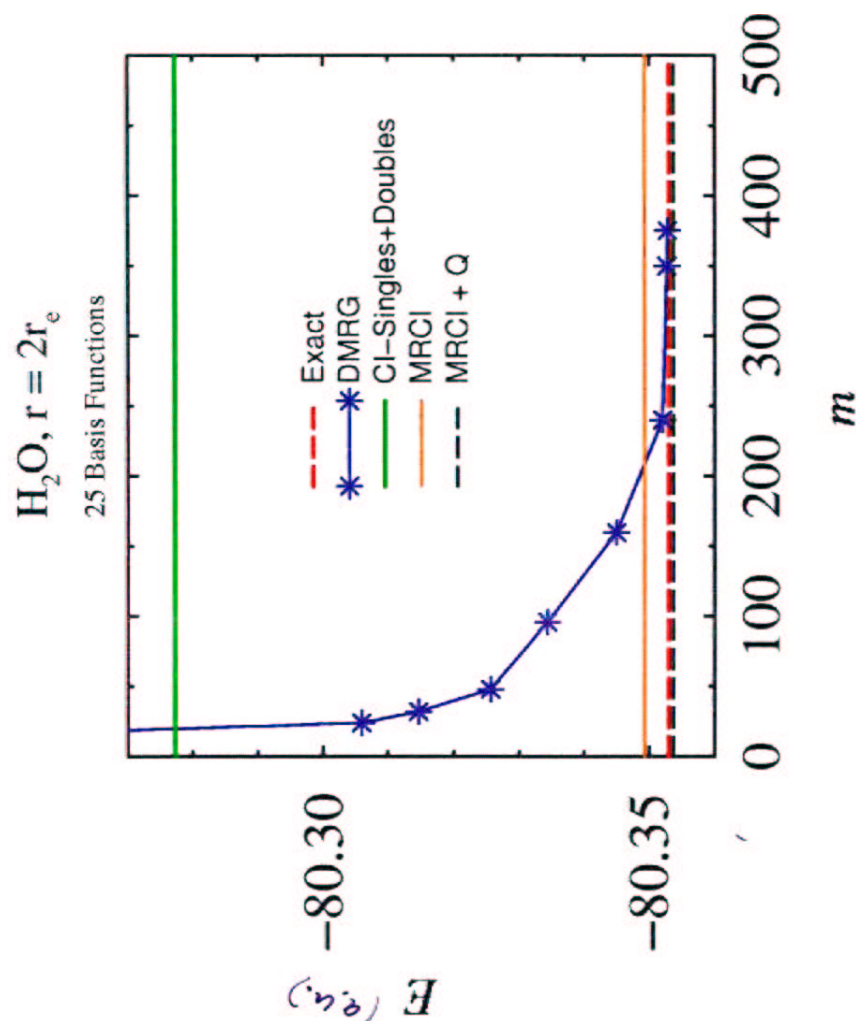
Final calculation time:  $\sim (N^2 m^3)N$   
Storage:  $\sim (N^2 m^2)N$  ( $N^2 m^2$  in core).



QC results from  
Bauschlicher + Taylor, 1986

HF = -84.84





### Numerical Canonical Transformations

Context: in using DMRG to treat larger systems, it becomes apparent that DMRG is inefficient: it treats high energy orbitals the same as levels near the Fermi level.

Is there a variation of DMRG that treats perturbative orbitals differently? I couldn't think of a good one.

Is there another RG approach that can remove the perturbative orbitals before DMRG is used? Yes, numerical canonical/unitary transformations.

### Flow equation method

Invented independently in 1994 by Wegner and by Glazek and Wilson.

$H$  evolves continuously, becoming more and more diagonal

$$\frac{dH(t)}{dt} = [A(t), H(t)]$$

where the generator  $A(t)$  is antihermitian and is taken to be

$$A(t) = [H_d(t), H(t)]$$



### Jacobi Canonical Diagonalization

Jacobi method: a numerical method for diagonalizing matrices. Rotate away each off-diagonal matrix element with a  $2 \times 2$  transformation matrix,  $H' = e^A H e^{-A}$ , where

$$\exp(A) = \exp \begin{pmatrix} 0 & \theta \\ -\theta & 0 \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix}$$

where we choose

$$\theta = \frac{1}{2} \tan^{-1} [2H_{ij} / (H_{ii} - H_{jj})]$$

In Jacobi Canonical Diagonalization, we do a similar procedure for the second quantized Hamiltonian. An off diagonal term is anything distinct from its Hermitian conjugate. For example, to remove

$$V = a c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{k\downarrow} c_{l\uparrow},$$

and its Hermitian conjugate, we construct the antihermitian operator

$$A = \theta(V - V^\dagger)/a$$

and rotate using

$$e^A H e^{-A} = H + [A, H] + \frac{1}{2!} [A, [A, H]] + \dots$$

where

$$\theta = \frac{1}{2} \tan^{-1} [2a / (E_i - E_j)].$$

We then repeat for all off diagonal terms we wish to remove, iterating, since each Jacobi rotation changes previously zeroed terms.

### Jacobi Canonical Diagonalization, continued

How do we implement this numerically?

Straightforward but completely general way: each  $c_{i\sigma}$  or  $c_{i\sigma}^\dagger$  stored using one byte, and one term is an array of bytes plus a floating point coefficient. Write subroutines to take commutators of terms, put in normal ordered form, ... (C++, could do in Mathematica).

Faster way: put in matrix form, but need to computer-generate the commutator loops (20,000 lines).

**Discarding terms:** transformations generate terms involving all numbers of particles. Simplest truncation rule: discard all 3+ particle terms.

**Which off-diagonal terms do we rotate away?** All terms? Severe problems with near degeneracies. Better choices:

1. Remove all terms which connect to the Hartree Fock ground state. Example: if

$$V = a c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{k\downarrow} c_{l\uparrow},$$

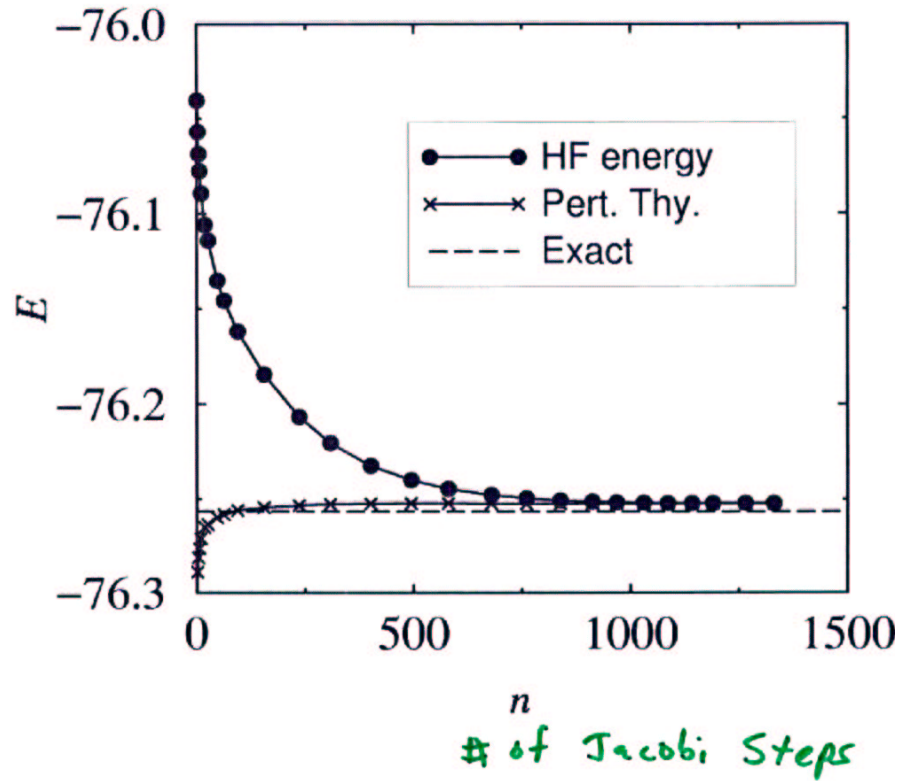
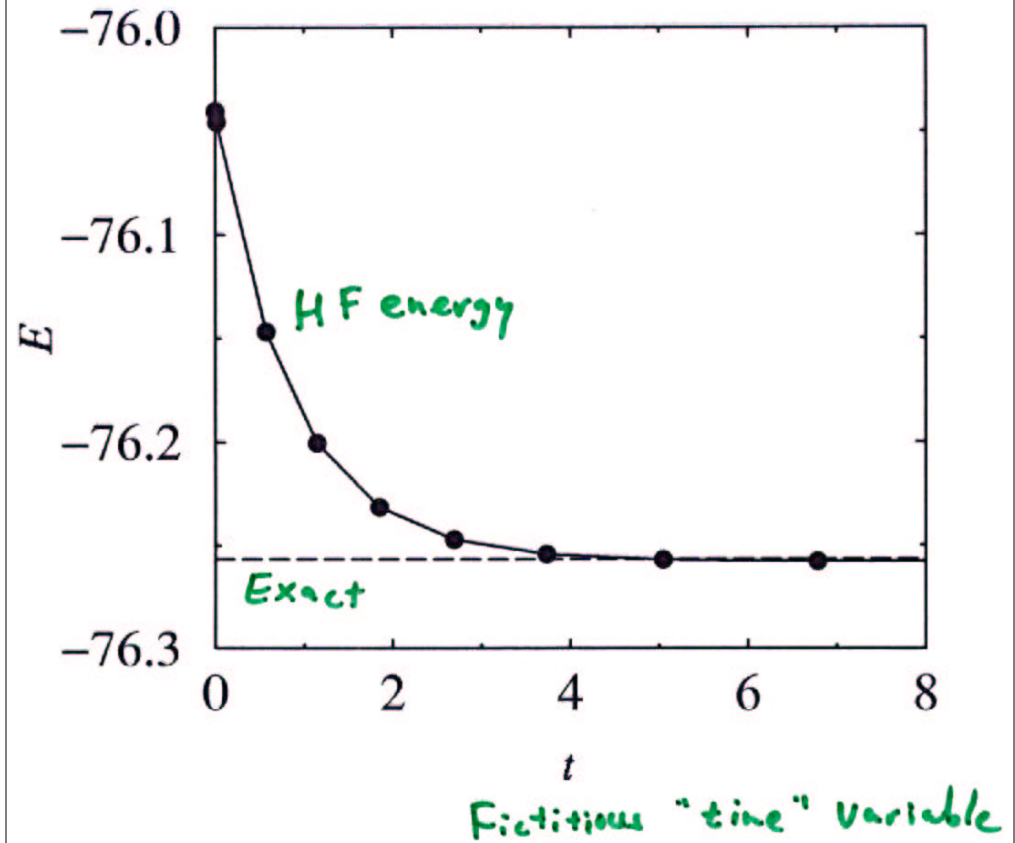
remove only if  $k$  and  $l$  are below Fermi level, and  $i$  and  $j$  are above (or vice-versa)

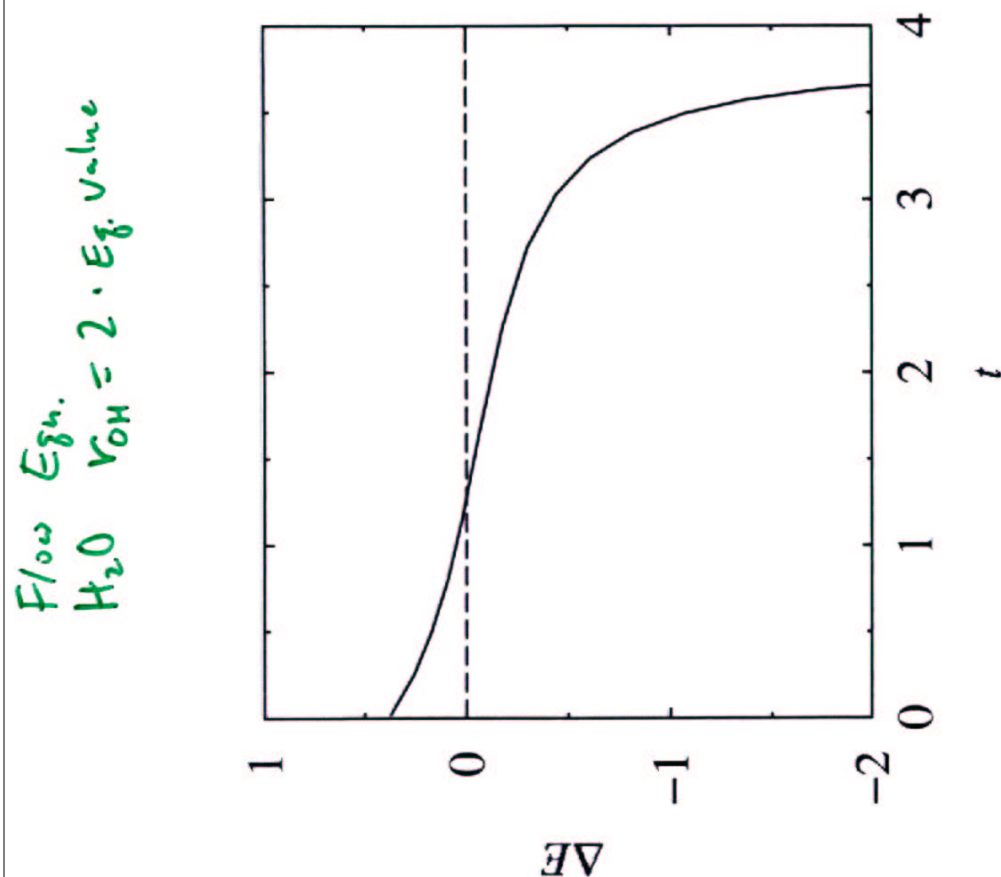
Result: for transformed  $H$ , HF ground state is exact ground state.

2. **To “integrate out” an orbital:** remove all terms which change the occupancy of that orbital ( $k$ ), i.e. which have a  $c_k$  or a  $c_k^\dagger$ , but not both.

Result:  $H$  commutes with  $n_{k\sigma}$ . Then we choose to consider only  $\langle n_{k\sigma} \rangle = 0$  sector, so discard the orbital and all terms involving it!

Jacobi CD

 $H_2O$ , Equil. geometry $N=25$ Flow Egn. Method  
 $H_2O$  Eq. geom.  
 $N=25$ 



### Combining canonical transformations and DMRG

Procedure: Apply flow equation method to remove indicated number of orbitals (farthest from Fermi level). Then apply DMRG on smaller remaining system (very accurate).

System:  $H_2O$ , with  $N = 25$  basis functions.  
 Truncation rule: discard all terms involving more than two particles.

| Orbitals<br>Removed | $\Delta E$ |
|---------------------|------------|
| 8                   | -0.0003    |
| 13                  | -0.0003    |
| 17                  | 0.016      |
| 20                  | 0.014      |
| 21                  | 0.012      |



## Conclusions

DMRG can be used for very accurate *ab initio* calculations of ground states of small molecules. Currently we are limited to 60 or 70 basis functions.

Numerical canonical transformations can be used to solve non-strongly-correlated molecules, and to remove most orbitals from strongly correlated systems.

The combination of the two methods is particularly powerful for quantum chemistry.

For the future: apply canonical transformation methods to derive models of strongly correlated systems.