Strong Electron Correlation

Paul W. Ayers

ayers@mcmaster.ca

Department of Chemistry & Chemical Biology; McMaster University

This result flows at once from the idea of a correlation, in virtue of which the two terms mutually imply each other, and are the reciprocal condition one of the other, a correlation of which the purest product is beauty. But experience does not offer an example of so perfect a correlation.

J. C. Friedrich von Schiller

The Electronic Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \sum_{i=1}^{N_{\text{electrons}}} \underbrace{-\frac{1}{2}\nabla_i^2}_{\substack{\text{electronic} \\ \text{kinetic energy}}} + \overset{\substack{\text{electron-nuclear} \\ \text{attraction potential}}}{v(\mathbf{r})} + \underbrace{\sum_{j=1}^{i-1}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\substack{\text{electron-electron} \\ \text{repulsion potential}}}$$

Energies are obtained as eigenvalues.

All other properties can be found from the eigenvectors.

Average-Potential Models: One Slater Determinant

$$\hat{H}_{\text{avg}} \Phi = \sum_{i \in \text{occ}} \varepsilon_i \Phi$$

average electron-electron potential of an electron at $\mathbf{r}_i$

$$\hat{H}_{\text{avg}} = \sum_{i=1}^{N_{\text{electrons}}} -\tfrac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) + w(\mathbf{r}_i)$$

"Electron Cloud"

Hartree-Fock

Kohn-Sham DFT

Example: Lithium Atom, $1s^2 2s^1$

<u>Born Postulate:</u> the probability distribution function for electrons is the square-magnitude of the wavefunction.

$$P_{Li}\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3\right) = \left|\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3\right)\right|^2$$

<u>Hartree Product:</u> Independent Particle Approximation.

$$P_3\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3\right) = p_{1s,\alpha}\left(\mathbf{r}_1\right) p_{1s,\beta}\left(\mathbf{r}_2\right) p_{2s,\alpha}\left(\mathbf{r}_3\right)$$

$$= \left|\psi_{1s}\left(\mathbf{r}_1\right)\alpha(1)\psi_{1s}\left(\mathbf{r}_2\right)\beta(2)\psi_{2s}\left(\mathbf{r}_3\right)\alpha(3)\right|^2$$

<u>Slater determinant:</u> Independent Particle Approximation but account for independent-particle statistics for fermions,

$$P_3\left(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3\right) = \left| \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}\left(\mathbf{r}_1\right)\alpha(1) & \psi_{1s}\left(\mathbf{r}_1\right)\beta(1) & \psi_{2s}\left(\mathbf{r}_1\right)\alpha(1) \\ \psi_{1s}\left(\mathbf{r}_2\right)\alpha(2) & \psi_{1s}\left(\mathbf{r}_2\right)\beta(2) & \psi_{2s}\left(\mathbf{r}_2\right)\alpha(2) \\ \psi_{1s}\left(\mathbf{r}_3\right)\alpha(3) & \psi_{1s}\left(\mathbf{r}_3\right)\beta(3) & \psi_{2s}\left(\mathbf{r}_3\right)\alpha(3) \end{vmatrix} \right|^2$$

Also works for nuclei and other fermions; replace determinant with permanent for bosons (which is problematic...).

One dominant electron configuration → the Slater determinant is a good starting point & existing methods work well.

Many important electron configurations → the orbital picture is invalid…the problem of strong correlation…

HF/DFT
CISD...
CCSD...
MPn

CASSCF (~10)
DMRG (~50)
MR-CI/CC

?????
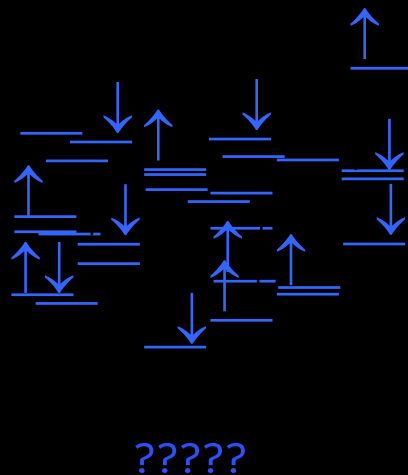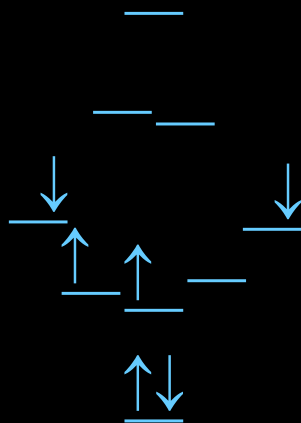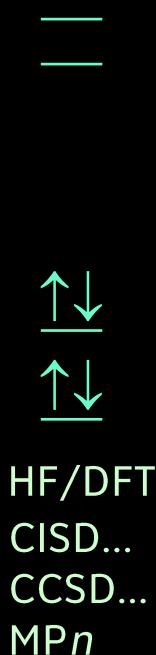
One dominant electron configuration → the Slater determinant is a good starting point & existing methods work well.

Many important electron configurations → the orbital picture is invalid…the problem of strong correlation…

| Single-reference	Near-degeneracy	Strong correlation
$n_i^{\text{frontier}} \approx \{0,1\}$	$n_i^{\text{frontier}} \sim 1/2$	$n_i^{\text{frontier}} \ll 1$
band gap $\gg V_{ee}$[valence]	band gap $\sim V_{ee}$[valence]	band gap $\ll V_{ee}$[valence]
Equilibrium structures	stretched bonds transition-states of rxns	Superconductors Large quantum dots
Saturated hydrocarbons	polyacenes; polynes; cumulenes	spin-frustrated systems Wigner crystal
closed-shell main-group molecules	transition-metal compounds, Cr_2, noninnocent ligands Open-shell molecules (esp. f-block and d-block elements)	Heavy-fermion materials Molecular magnets Kondo state quantum phase transitions
noninteracting electrons	Hubbard & PPP models	Richardson & Heisenberg models

Symmetry-Breaking in Mean-Field Models

Real chemical systems possess certain symmetries, defined by operators that commute with the Hamiltonian

o Total-spin and spin-orientation (in absence of magnetic fields)
o Number of electrons
o Spatial-symmetry/angular momentum (in symmetric systems)
o complex conjugation (invariance to phases)
o particle-hole symmetry (at half-filling)
o ….

Allowing these symmetries to "break" extends mean-field models beyond the normal domain of validity but….

o Dynamic correlation is missing (almost by definition)
o Experiments (spectroscopy) measure states with good symmetry.
o Tyranny of the energy: the eigenfunctions are qualitatively incorrect, so while the energy may be accurate, other properties may be modelled only very inaccurately.

  • e.g., poor predictions of magnetic properties for spin-symmetry-broken wavefunctions.

Example: Spatial-symmetry breaking in Jahn-Teller transition-metal complexes, 1-dimensional chains, antiaromatic systems, Carbon dimer (cf. figure),...
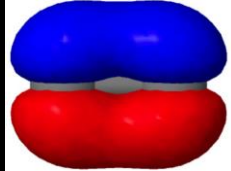
Example: Coulson-Fisher (spin-sym breaking)
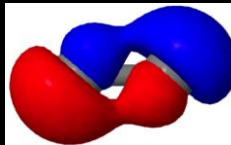
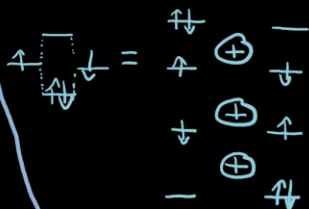MO theory / Single Slater determinant

$$\phi_1 = \phi_{left}(1) + \phi_{right}(1)$$

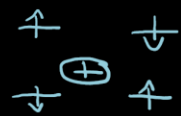$$\Psi = \phi_1(1)\,\phi_1(2)\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

VB theory

$$\Psi = \begin{bmatrix} \phi_{left}(1)\,\phi_{right}(2) \\ + \phi_{right}(1)\,\phi_{left}(2) \end{bmatrix} \cdot [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$E_{UHF} < E_{RHF}$

Coulson-Fisher Point

Spin-Recoupling Region

$E_{UHF} = E_{RHF}$

E

R

This occurs due to the presence of near degeneracy, and especially nearly-degenerate states with different spin/spatial symmetry.

$$\left| \Phi_{\substack{\text{mean-field} \\ \text{sym. broken}}} \right\rangle = \sum_{\mathcal{S}} c_{\mathcal{S}} \left| \Psi_{\mathcal{S}} \right\rangle$$

$$\left| \Psi_{\mathcal{S}} \right\rangle = \hat{P}_{\mathcal{S}} \left| \Phi_{\substack{\text{mean-field} \\ \text{sym. broken}}} \right\rangle$$

Symmetry can be restored by projection; the symmetry-projected state is *not* mean-field but is often quite good because it includes only the "best" lowest energy state. I.e.,

$$\left\langle \Phi_{\substack{\text{mean-field} \\ \text{sym. broken}}} \left| \hat{H} \right| \Phi_{\substack{\text{mean-field} \\ \text{sym. broken}}} \right\rangle = \sum_{\mathcal{S},\mathcal{S}'} c_{\mathcal{S}}^{*} c_{\mathcal{S}'} \left\langle \Psi_{\mathcal{S}} \left| \hat{H} \right| \Psi_{\mathcal{S}'} \right\rangle$$

$$= \sum_{\mathcal{S}} \left| c_{\mathcal{S}} \right|^{2} \left\langle \Psi_{\mathcal{S}} \left| \hat{H} \right| \Psi_{\mathcal{S}} \right\rangle = \sum_{\mathcal{S}} \left| c_{\mathcal{S}} \right|^{2} E_{\mathcal{S}}$$

$$\geq E_{\mathcal{S}_{\text{g.s.}}}$$

Beyond the Average Potential: Many Electron Configurations
(Many Slater Determinants)

$$\hat{H}_{\text{electrons}} = \sum_{i=1}^{N_{\text{electrons}}} -\tfrac{1}{2}\nabla_i^2 + v(\mathbf{r}) + \sum_{j=1}^{i-1} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

$$\Psi = c_0\Phi_0 + c_1\Phi_1 + c_2\Phi_2 + \cdots$$

"Electron Droplets"

Configuration Interaction

Curse of Dimension: The number of electron configurations (Slater determinants) grows exponentially as the number of electrons increases

	# of e$^-$	# of Sl. Dets. (cc-pVTZ)
He	2	196
Be	4	189,225
Ne	10	20,307,960,036
Mg	12	1,808,766,769,216
Ar	18	2,751,134,255,977,536

<u>Conventional Strategy #1:</u> Single-reference theories.
(Nobel Prize 1998; John Pople)

Use a single Slater determinant as a starting point; add corrections for neglected effects.

- Highly effective when a single Slater determinant is a good qualitative description of the system.
- Systematically improvable but with exponentially increasing cost
- Examples:
  - many-body perturbation theory
  - limited configuration interaction
  - coupled cluster (cumulant) expansion;...
- Qualitatively ineffective for strong correlation.
  - electron-electron repulsion energy is similar to the splitting between frontier orbitals (orbitals near the Fermi level).
  - ...many important electron configurations.
  - ...impossible to assign "occupied" and "unoccupied" orbitals to define an adequate reference determinant.

Since I have confined my imagination to the margin...those changes may be safely offered...
Samuel Johnson

Conventional Strategy #2: Alternative Descriptor Approach.
(Nobel Prize 1998; Walter Kohn)

Use a simpler descriptor that nonetheless suffices to describe all properties of an electronic system.

- Computationally Affordable.
- Theoretically exact, but "existence theorems" give few hints for practical computational methods.
- Examples:
  o Density-functional theory & Electron-Distribution Functional Th.
  o Density-matrix approaches
  o Electron-propagator (Green's function) methods (sometimes)
- Not robust: must select "right method for right problem"
- Qualitatively ineffective for strong correlation.
  o Models used to design practical computational schemes are rarely effective for strongly correlated systems.

> ...theories which are restrained by no reference to existing analogies, and in which a desire is manifested to cut, rather than patiently to untie, the Gordian knot.
> Charles Lyell

$\gamma(\boldsymbol{r},\boldsymbol{r}') \quad \Gamma_2(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{r}_1',\boldsymbol{r}_2') \, \Gamma_3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3;\boldsymbol{r}_1',\boldsymbol{r}_2',\boldsymbol{r}_3') \quad \Gamma_4 \quad \text{full-CI}$

$\rho(\boldsymbol{r}) \quad \rho_2(\boldsymbol{r},\boldsymbol{r}') \quad \rho_3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) \quad \rho_4(\boldsymbol{r}_1,\ldots\boldsymbol{r}_4) \quad \rho_N=|\Psi|^2 \quad \Psi$

HF,CIS   CCSD, etc. CCSDT, etc. CCSDTQ, etc. full-CI

Science strives to make the new
intelligible in terms of the familiar.
                          Baruch Spinoza

14

Conventional Strategy #3: Direct Assault

Use "trickery" to represent an exponentially complex wavefunction.

- Must exploit simplifying features of "real" electronic systems.

- Examples:
    - Truncation of the CI expansion based on chemical and/or mathematical considerations.
    - Factorization of the wavefunction.
    - Efficient reparameterization of the wavefunction.
    - Monte-Carlo techniques.

- Requires inspiration and "domain knowledge."

It should always be borne in mind that when part is modified, so will be other parts, through certain dimly seen causes … which lead to the many mysterious cases of correlation, which we do not in the least understand.

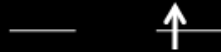Charles Darwin

Second Quantization

A Slater Determinant:

$$\left| \phi_i \phi_j \phi_k \phi_l \right| = \left| \phi_i \phi_j \phi_k \phi_l \right\rangle = a_i^+ a_j^+ a_k^+ a_l^+ \left| \theta \right\rangle$$

Creators of Electrons

Annihilators of Electrons

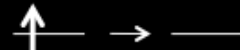$a_i^+ \left| q \right\rangle = \left| f_i \right\rangle$
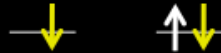
$a_i^+ \left| f_i \right\rangle = 0$

$a_i^+ \left| f_j \right\rangle = \left| f_i f_j \right\rangle$
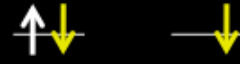
$a_i \left| q \right\rangle = 0$

$a_i \left| f_i \right\rangle = \left| q \right\rangle$

$a_i \left| f_i f_j \right\rangle = \left| f_j \right\rangle$

Pauli principle enforced by construction:

$$a_i^+ a_j + a_j a_i^+ = \delta_{ij} \qquad a_i a_j = -a_j a_i \qquad a_i^+ a_j^+ = -a_j^+ a_i^+$$

1-body and 2-body operators compactly expressed:

$$\hat{h} = \sum_{i,j} h_{ij} a_i^+ a_j \qquad \hat{V} = \sum_{i,j,k,l} g_{ijkl} a_i^+ a_j^+ a_l a_k$$

Use a Slater determinant as an initial guess.....

Unrestricted Hartree-Fock

$$\left|\Phi_{\text{UHF}}\right\rangle = a_1^\dagger a_2^\dagger \ldots a_N^\dagger \left|\theta\right\rangle \qquad N = \text{\# of electrons}$$

Singly-excited Slater determinant; doubly-excited Slater det.;...

$$\left|\Phi_i^a\right\rangle = a_a^+ a_i \left|\Phi_{\text{UHF}}\right\rangle \qquad\qquad \left|\Phi_{ij}^{ab}\right\rangle = a_a^+ a_b^+ a_j a_i \left|\Phi_{\text{UHF}}\right\rangle$$

$$i,j \in \text{occ} \quad \left(1 \le i \le N\right) \qquad a,b \in \text{virt} \quad \left(a > N\right)$$

Linear combinations of Slater determinants.

Configuration Interaction (Linear Combination of Slater Dets.)

$$\left|\Psi_{\text{CISDT}\cdots}\right\rangle = \left(1 + \overbrace{\underbrace{\sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} c_i^a a_a^+ a_i}_{\text{CI-Singles (CIS)}} + \sum_{\substack{i,j \in \text{occ} \\ a,b \in \text{virt}}} c_{ij}^{ab} a_a^+ a_b^+ a_j a_i}^{\text{CI-Singles \& Doubles (CISD)}} + \sum_{\substack{i,j,k \in \text{occ} \\ a,b,c \in \text{virt}}} c_{ijk}^{abc} a_a^+ a_b^+ a_c^+ a_k a_j a_i + \cdots\right) \left|\Phi_{\text{UHF}}\right\rangle$$

Coupled Cluster. Product Form.

$$|\Psi_{\text{CCSDT}\cdots}\rangle = \left(\overbrace{\overbrace{\prod_{\substack{i\in\text{occ} \\ a\in\text{virt}}} \left(1+t_i^a a_a^+ a_i\right)}^{\text{CC-Singles (CCS)}} \prod_{\substack{i,j\in\text{occ} \\ a,b\in\text{virt}}} \left(1+t_{ij}^{ab} a_a^+ a_b^+ a_j a_i\right)}^{\text{CC-Singles \& Doubles (CCSD)}} \prod_{\substack{i,j,k\in\text{occ} \\ a,b,c\in\text{virt}}} \left(1+t_{ijk}^{abc} a_a^+ a_b^+ a_c^+ a_k a_j a_i\right) + \cdots \right) |\Phi_{\text{UHF}}\rangle$$

$$= \exp\left(1 + \underbrace{\underbrace{\sum_{\substack{i\in\text{occ} \\ a\in\text{virt}}} t_i^a a_a^+ a_i}_{\text{CCS}} + \sum_{\substack{i,j\in\text{occ} \\ a,b\in\text{virt}}} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i}_{\text{CCSD}} + \sum_{\substack{i,j,k\in\text{occ} \\ a,b,c\in\text{virt}}} t_{ijk}^{abc} a_a^+ a_b^+ a_c^+ a_k a_j a_i + \cdots \right) |\Phi_{\text{UHF}}\rangle$$

Occupation Number Representation

For a system with *K* spin-orbitals, choosing:

$$\left(a_k^+\right)^{m_k} \equiv \begin{cases} m_k = 1 & a_k^+; \text{ occupy } k^{\text{th}} \\ m_k = 0 & 1; \text{ multiply by } 1 \end{cases}$$

Full-CI: sum over all possible ways of occupying *N* orbitals

$$\left|\Psi_{\text{FCI}}\right\rangle = \sum_{\left\{m_1,m_2,\ldots m_K \middle| \substack{m_k \in \{0,1\} \\ N = \sum_{k=1}^{K} m_k}\right\}} c^{(m_1 m_2 \ldots m_K)} \left(a_1^+\right)^{m_1} \left(a_2^+\right)^{m_2} \left(a_3^+\right)^{m_3} \cdots \left(a_K^+\right)^{m_K} \left|\theta\right\rangle$$

There is no dependence on a reference determinant in the occupation number representation....

Matrix Product States

$$a_{\kappa_1}^{(n_{1\uparrow}n_{1\downarrow})}[1]\,a_{\kappa_1\kappa_2}^{(n_{2\uparrow}n_{2\downarrow})}[2]\,a_{\kappa_2\kappa_3}^{(n_{3\uparrow}n_{3\downarrow})}[3]\,a_{\kappa_3\kappa_4}^{(n_{4\uparrow}n_{4\downarrow})}[4]\,a_{\kappa_4\kappa_5}^{(n_{5\uparrow}n_{5\downarrow})}[5]\,a_{\kappa_5}^{(n_{6\uparrow}n_{6\downarrow})}[6]$$

$$\left|\Psi_{\text{FCI}}\right\rangle = \sum_{\left\{m_k \in \{0,1\}; N = \sum_{k=1}^{K} m_k\right\}} c^{(m_1 m_2 \ldots m_K)} \left(a_1^+\right)^{m_1} \left(a_2^+\right)^{m_2} \left(a_3^+\right)^{m_3} \cdots \left(a_K^+\right)^{m_K} \left|\theta\right\rangle$$

There are $O(2^K)$ CI coefficients. We can factor them:

$$c^{(m_1 m_2)} = \sum_{\ell=1}^{2} {}^{1}a_\ell^{(m_1)} \cdot {}^{2}a_\ell^{(m_2)}$$

$$\overbrace{m^{(ij)} = \sum_{\ell=1}^{n} a_\ell^{(i)} b_\ell^{(j)}}^{\text{Schmidt decomposition}}; \quad \overbrace{h_{ij} = \sum_{\ell=1}^{n} \lambda_\ell u_\ell^{(i)} v_\ell^{(j)}}^{\substack{\text{eigenvalue decomposition} \\ \mathbf{H}\mathbf{v}_\ell = \lambda_\ell \mathbf{v}_\ell \quad \mathbf{u}_\ell^T \mathbf{H} = \lambda_\ell \mathbf{u}_\ell^T}}$$

$$c^{(m_1 m_2 m_3)} = \sum_{\ell_1=1}^{2} \sum_{\ell_2=1}^{2} {}^{1}a_{\ell_1}^{(m_1)} \cdot {}^{2}a_{\ell_1 \ell_2}^{(m_2)} \cdot {}^{3}a_{\ell_2}^{(m_3)}$$

$$c^{(m_1 m_2 m_3 m_4)} = \sum_{\ell_1=1}^{2} \sum_{\ell_2=1}^{4} \sum_{\ell_3=1}^{2} {}^{1}a_{\ell_1}^{(m_1)} \cdot {}^{2}a_{\ell_1 \ell_2}^{(m_2)} \cdot {}^{3}a_{\ell_2 \ell_3}^{(m_3)} \cdot {}^{4}a_{\ell_3}^{(m_4)}$$

$$c^{(m_1 m_2 \cdots m_j \cdots m_{K-1} m_K)}$$

$$= \sum_{\ell_1=1}^{2} \sum_{\ell_2=1}^{4} \cdots \sum_{\ell_j=1}^{\min\left(2^j, 2^{K-j}\right)} \cdots \sum_{\ell_{K-2}=1}^{4} \sum_{\ell_{K-1}=1}^{2} {}^{1}a_{\ell_1}^{(m_1)} \cdot {}^{2}a_{\ell_1 \ell_2}^{(m_2)} \cdots {}^{j}a_{\ell_{j-1} \ell_j}^{(m_j)} \cdots {}^{K-1}a_{\ell_{K-2} \ell_{K-1}}^{(m_{K-1})} \cdot {}^{K}a_{\ell_{K-1}}^{(m_K)}$$

When one does a singular-value decomposition or an eigenvalue decomposition of a matrix, it is common to make a low-rank approximation:

$$\mathbf{M} \approx \sum_{\sigma_\ell \geq \varepsilon} \sigma_\ell \mathbf{u}_\ell \mathbf{v}_\ell^T = \sum_{\ell=1}^{D \ll n} \sigma_\ell \mathbf{u}_\ell \mathbf{v}_\ell^T \qquad\qquad \mathbf{M} \approx \sum_{|\lambda_\ell| \geq \varepsilon} \lambda_\ell \mathbf{u}_\ell \mathbf{v}_\ell^T = \sum_{\ell=1}^{D \ll n} \lambda_\ell \mathbf{u}_\ell \mathbf{v}_\ell^T$$

Similarly, truncate the factorization of the CI coefficients:

$$c^{\left(m_1 m_2 \cdots m_j \cdots m_K\right)} \approx \sum_{\ell_1=1}^{2} \sum_{\ell_2=1}^{4} \cdots \sum_{\ell_j=1}^{\min\left(2^j, 2^{K-j}, D\right)} \cdots \sum_{\ell_{K-1}=1}^{2} {}^1 a_{\ell_1}^{(m_1)} \cdot {}^2 a_{\ell_1 \ell_2}^{(m_2)} \cdots {}^j a_{\ell_{j-1} \ell_j}^{(m_j)} \cdots {}^K a_{\ell_{K-1}}^{(m_K)}$$

Keep track of the "largest neglected weight" to control the error in the decomposition. This is the matrix product state. It is usually optimized using the density matrix renormalization group (DMRG) algorithm.

Note: The number of variational parameters is decreased from $O(2^K)$ to $O(KD^2)$. This is much cheaper....

This recovers full-CI as $D \rightarrow \infty$. To get there, we extrapolate versus the maximum discarded weight from the matrix decomposition. Computational Cost $O(K^3 D^3)$
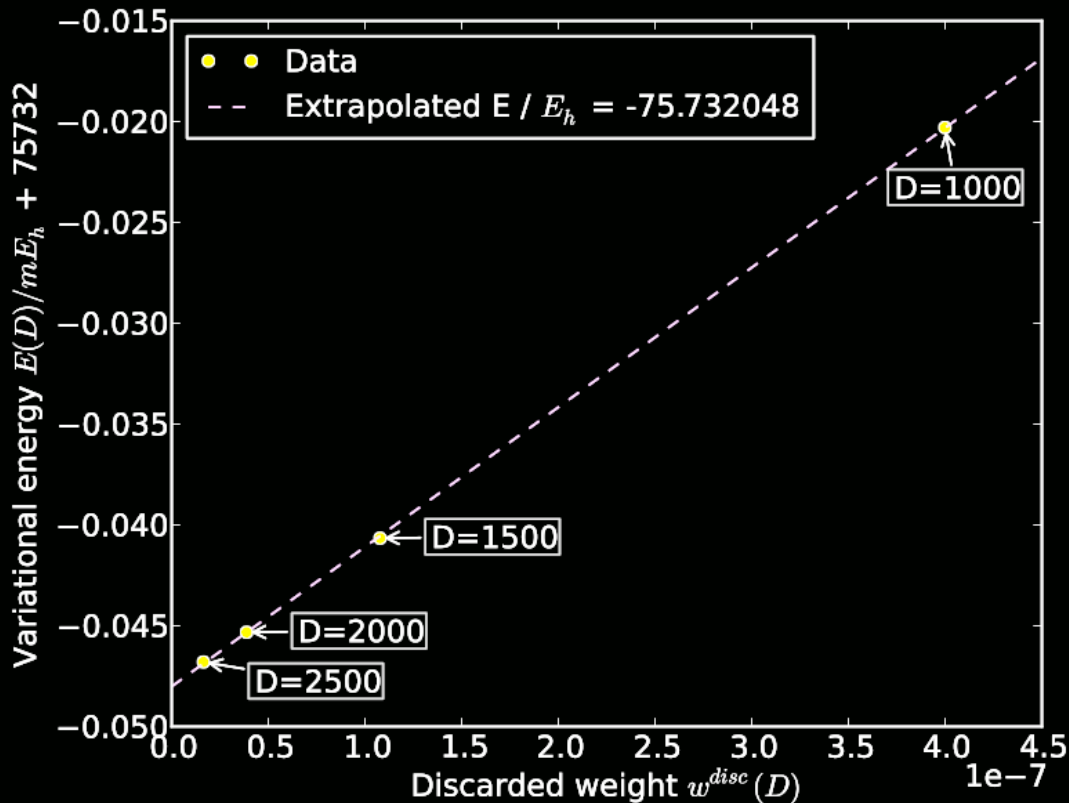
DMRG is usually performed using spatial orbitals. With "overloaded" notation, for a system with L spatial orbitals:

$$\left(o_j^+\right)^{\mu_j} \equiv \begin{cases} \mu_j = 3 & a_{j\alpha}^+ a_{j\beta}^+ \\ \mu_j = 2 & a_{j\beta}^+ \\ \mu_j = 1 & a_{j\alpha}^+ \\ \mu_j = 0 & 1 \end{cases}$$

The full-CI wavefunction is:

$$\left|\Psi_{\text{FCI}}\right\rangle = \sum_{\left\{\mu_j \in \{0,1,2,3\}; N = \sum_{\mu_j = \{1,2\}}^{L}(1) + \sum_{\mu_j = 3}^{L}(2)\right\}} c^{\left(\mu_1 \mu_2 \ldots \mu_L\right)} \left(o_1^+\right)^{\mu_1} \left(o_2^+\right)^{\mu_2} \cdots \left(o_L^+\right)^{\mu_L} \left|\theta\right\rangle$$

And the corresponding matrix product state is:

$$c^{\left(\mu_1 \mu_2 \cdots \mu_j \cdots \mu_L\right)} \approx \sum_{\ell_1 = 1}^{4} \sum_{\ell_2 = 1}^{16} \cdots \sum_{\ell_j = 1}^{\min\left(4^j, 4^{L-j}, D\right)} \cdots \sum_{\ell_{L-1} = 1}^{4} {}^1 a_{\ell_1}^{(\mu_1)} \cdot {}^2 a_{\ell_1 \ell_2}^{(\mu_2)} \cdots {}^j a_{\ell_{j-1} \ell_j}^{(\mu_j)} \cdots {}^L a_{\ell_{L-1}}^{(\mu_L)}$$

- The matrix product state is a parameterization of the full-CI wavefunction using only a polynomial number of unknowns.
  - But there can be a hidden exponential prefactor, as the number of retained states, D, may diverge exponentially.

- <u>Key Idea:</u> DMRG omits electron configurations that are less-important, using a "generalized" singular value decomposition.

- <u>Limitation:</u> Without further tricks, the method is limited to ~50 electrons in ~100 spatial orbitals.

- <u>Limitation:</u> Reliable calculations require extrapolation to the basis-set limit.

White, <u>Phys. Rev. Lett.</u> 69, 2863 (1992).

Chan & M. Head-Gordon, <u>J. Chem. Phys.</u> 116, 4462 (2002).

Östlung & Rommer, <u>Phys. Rev. Lett.</u> 75, 3537 (1995).

Olivares-Amaya, Hu, Nakatani, Sharma, Yang, Chan, <u>J. Chem. Phys.</u> 142, 034102 (2015).

Szalay, Pfeffer, Murg, Barcza, Verstraete, Schneider, Legeza <u>Int. J. Quantum Chem.</u> 115, 1342 (2015)

Wouters, Poelman, Ayers, Van Neck <u>Comp. Phys. Comm.</u> 185, 1501 (2014).

https://github.com/SebWouters/CheMPS2

Replace configurations of electrons with configurations of electron pairs.

Build wavefunctions not from orbitals (1e⁻ states) but two-electron states.

- Strong correlations from electron pairing (superconductivity, etc.) are automatically included this way.

A two-electron state is called a geminal. It is generated by:

$$G_p^+ = \sum_{i,j=1}^{K} c_{ij}^{(p)} a_i^+ a_j^+$$

so the wavefunction then has the form,

$$\left| \Psi \right\rangle = G_1^+ G_2^+ \cdots G_{N/2}^+ \left| \theta \right\rangle$$

Hurley, Lennard-Jones, & Pople, <u>Proc. R. Soc. London</u> vA220, 446 (1953).
Parr, Ellison, & Lykos, <u>J. Chem. Phys.</u> v24, 1106 (1956).
Surjan, Szabados, Jeszenszki, & Zoboki, <u>J. Math. Chem.</u> v50, 534 (2012).

There is a unitary transformation that allows us to rewrite the geminal in natural-orbital representation. For a singlet state:

$$G_p^+ = \sum_{i,j=1}^{K} c_{ij}^{(p)} a_i^+ a_j^+ = \sum_{i=1}^{L} c_i^{(p)} a_{i\alpha}^+ a_{i\beta}^+$$

The antisymmetric product of interacting geminals (APIG) is,

$$\left| \Psi_{\text{APIG}} \right\rangle = \prod_{p=1}^{N/2} \left(\sum_{i=1}^{L} c_i^{(p)} a_{i\alpha}^+ a_{i\beta}^+ \right) \left| \theta \right\rangle$$

This does *not* require a reference Slater determinant. In the occupation-number representation:,

$$\left| \Psi_{\text{APIG}} \right\rangle = \sum_{\left\{ \mu_j = \{0,1\} \middle| N = \sum_{j=1}^{L} 2\mu_j \right\}} \left| \mathbf{C}(\boldsymbol{\mu}) \right|^+ \left(a_{1\alpha}^+ a_{1\beta}^+ \right)^{\mu_1} \left(a_{2\alpha}^+ a_{2\beta}^+ \right)^{\mu_2} \cdots \left(a_{L\alpha}^+ a_{L\beta}^+ \right)^{\mu_L} \left| \theta \right\rangle$$

The expansion coefficients for the Slater determinants are *permanents* of the occupied orbitals coefficients, $\left| c_j^p \right|^+_{\substack{p=1\ldots N/2 \\ \mu_j=1}}$

Silver, J. Chem. Phys. v50, 5108 (1969); v52, 299 (1970).

Mathematics Trick

There are certain matrices whose permanents are easy to evaluate.

$$c_{i,p} = \frac{1}{a_p \varepsilon_i + b_i \lambda_p}$$

Then,

$$\left\| \left[c_{ip} \right] \right\|^+ = \frac{\left\| \left[c_{ip}^2 \right] \right\|}{\left\| \left[c_{ip} \right] \right\|}$$

C.W. Borchardt, "Bestimmung der symmetrischen Verbindungen vermittelst ihrer erzeugenden Funktion," Crelle's Journal, 53, 193-198 (1855).

Physics Trick

Use the "weak" formulation of the eigenvalue problem. Project the Schrödinger equation against Slater determinants:

$$\left\langle \Phi \middle| \hat{H} \middle| \Psi \right\rangle = E \left\langle \Phi \middle| \Psi \right\rangle \qquad \forall \Phi$$

We usually choose the project against just the pair excitations,

$$\left\langle \hat{H} \Phi_0 \middle| \Psi \right\rangle = E \left\langle \Phi_0 \middle| \Psi \right\rangle$$

$$\left\langle \hat{H} \Phi_{i\bar{i}}^{a\bar{a}} \middle| \Psi \right\rangle = E \left\langle \Phi_{i\bar{i}}^{a\bar{a}} \middle| \Psi \right\rangle$$

With this choice, there are other efficient geminal forms that can be used too.

Limacher, Ayers, Johnson, De Baerdemacker, Van Neck, and Bultinck, J. Chem. Theory Comp. v9, 1394 (2013).

Johnson, Ayers, Limacher, De Baerdemacker, Van Neck, and Bultinck, Comput. Theor. Chem. v1003, 101 (2013).

Example: Carbon Dimer (C_2). Hard because *lots* of low-lying states.
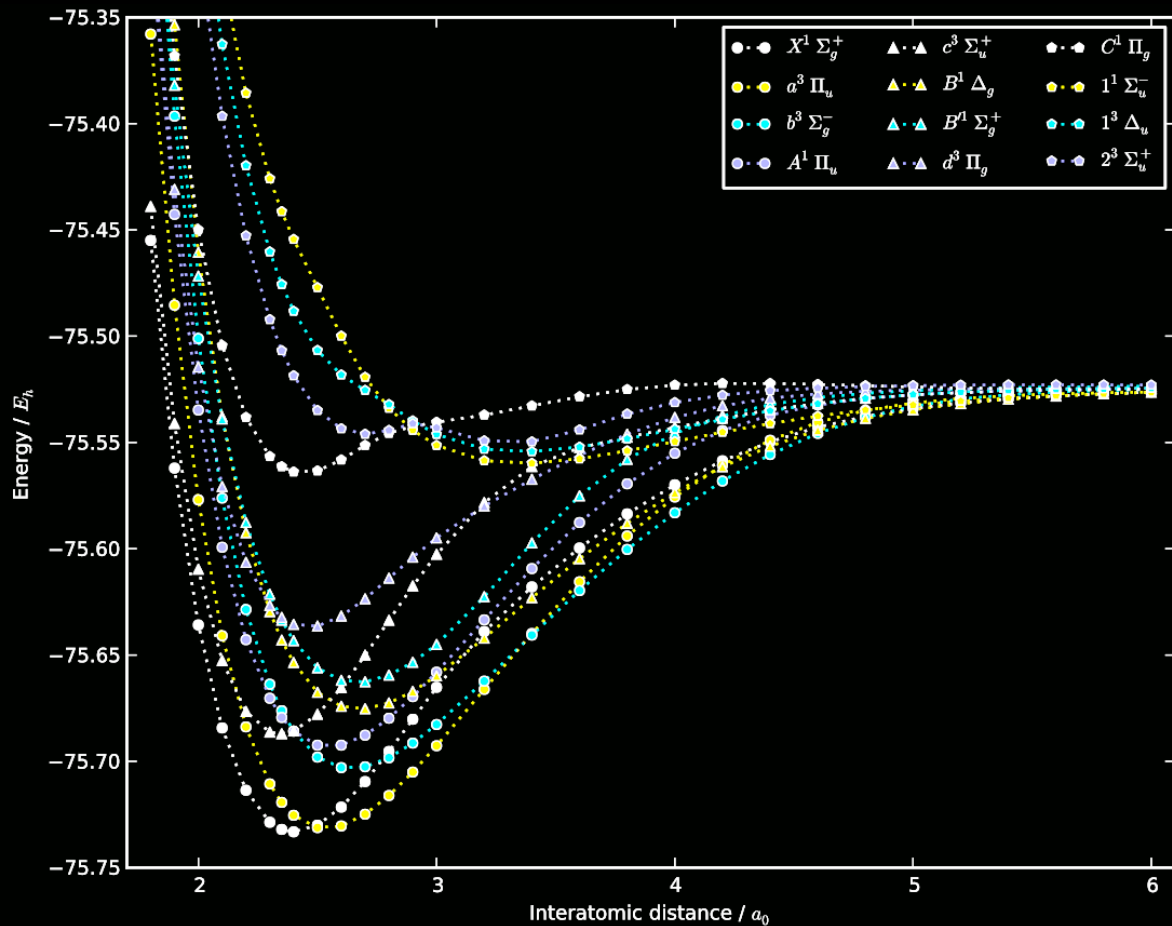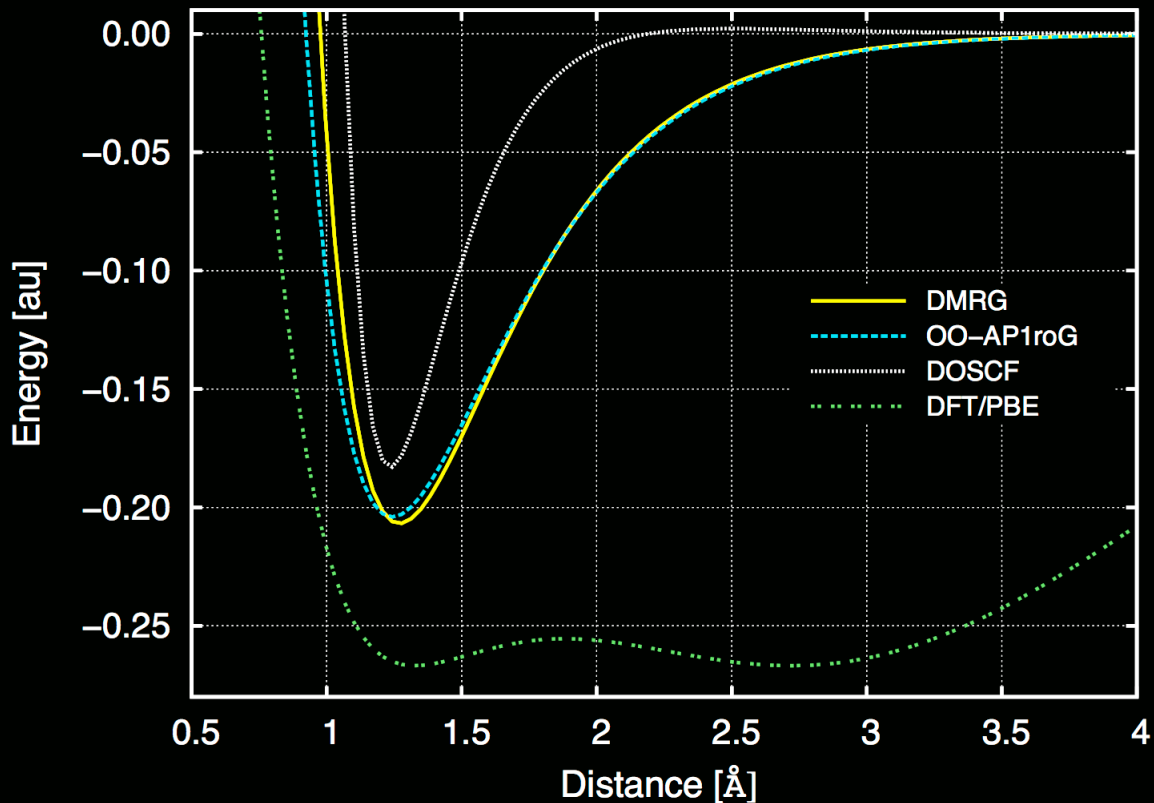
Tecmer,Boguslawski,Johnson,Limacher,Johnson,Chan,Verstraelen,Ayers J. Phys. Chem. A 118, 9058 (2014).
http://theochem.github.io/horton/

H$_{50}$ (Symmetric Stretch)
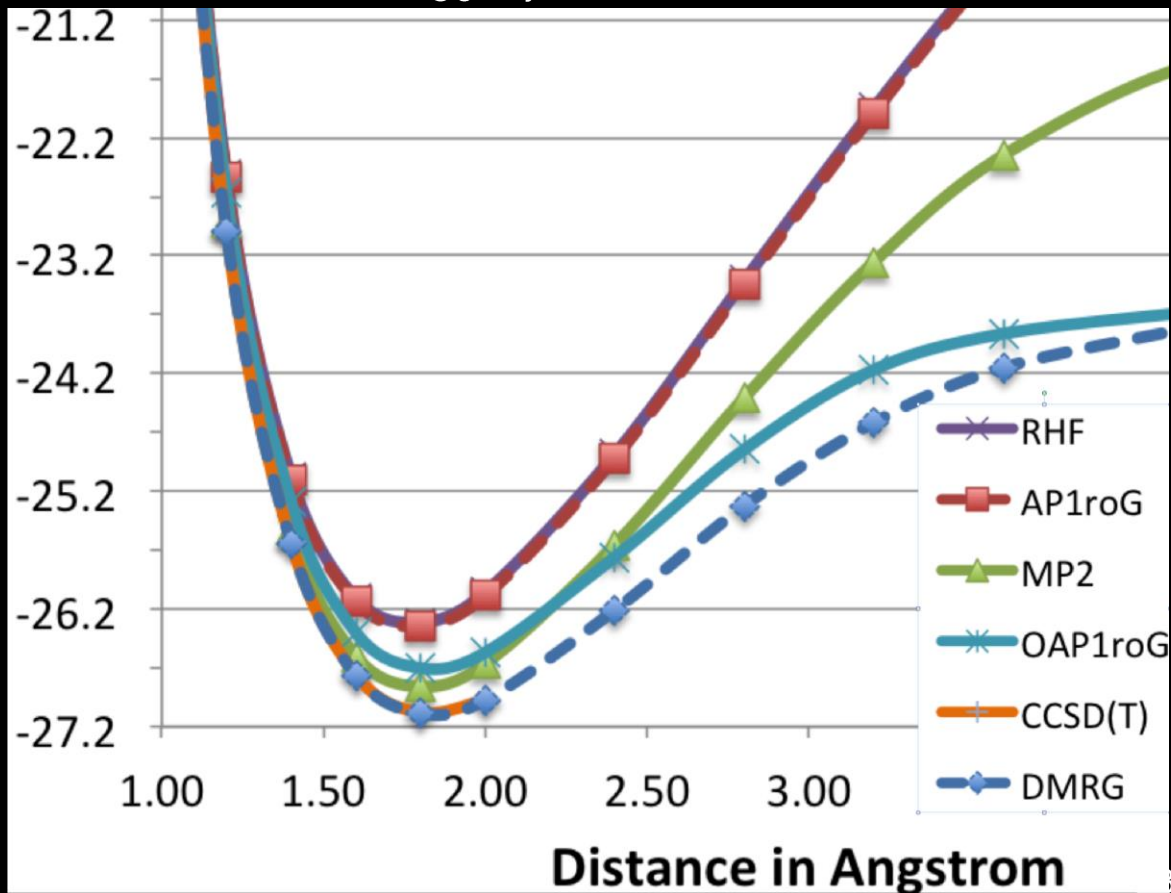
- The geminal product form captures most strong correlation effects.
  - It is a mean-field method for pairs, and thus very fast. (Potentially thousands of electrons.)
  - But there can be a hidden exponential prefactor in cases where this form is qualitatively incorrect.

- Key Idea: Build your wavefunction from electron pair quasiparticles, not quasi-independent electrons.

- Limitation: The method may not work well when the dominant strong-correlation effect is not based on electron-pairing.

- Limitation: The method does not approach full-CI in some limit. It is limited to even numbers of electrons, and (partly) neglects weak correlations.

Surján. In Correlation and localization Springer, Berlin, 1999 (pp. 63-88).
Limacher, et al. J. Chem. Th. Comp. 2013; 9:1394-401.
Johnson, et al. Comp. Theor. Chem. 2013; 1003:101-13.
Boguslawski, et al. Phys. Rev. B. 2014; 89:201106.
Stein, Henderson, Scuseria. J. Chem. Phys. 2014; 140:214113.

- *If* you suspect there might be more than one important electron configuration, be very careful!!
  - o CASSCF/DMRG/Multireference Methods.
  - o Geminals(?) Too early to know….
  - o Must include excitations to all orders.
- ….*or* just ignore the problem and hope for the best. It's what most people do.

…where ignorance is bliss, 'tis folly to be wise.

Thomas Gray
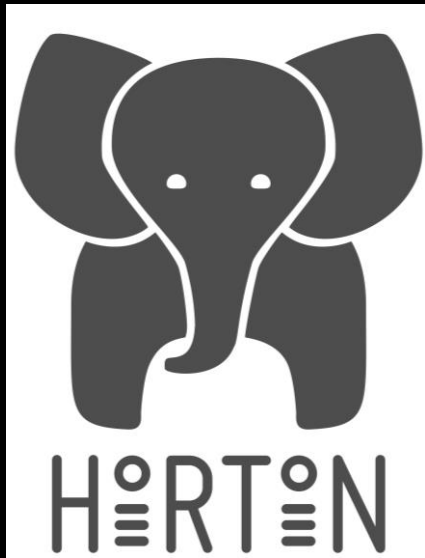
Helpful
Open-Source
Research
TOol for
N-fermion Systems

Toon
Verstraelen

http://theochem.github.io/horton