

Mean Field Methods for Electron Pairs: Some New Twists on an Old Approach to Strong Electron Correlation

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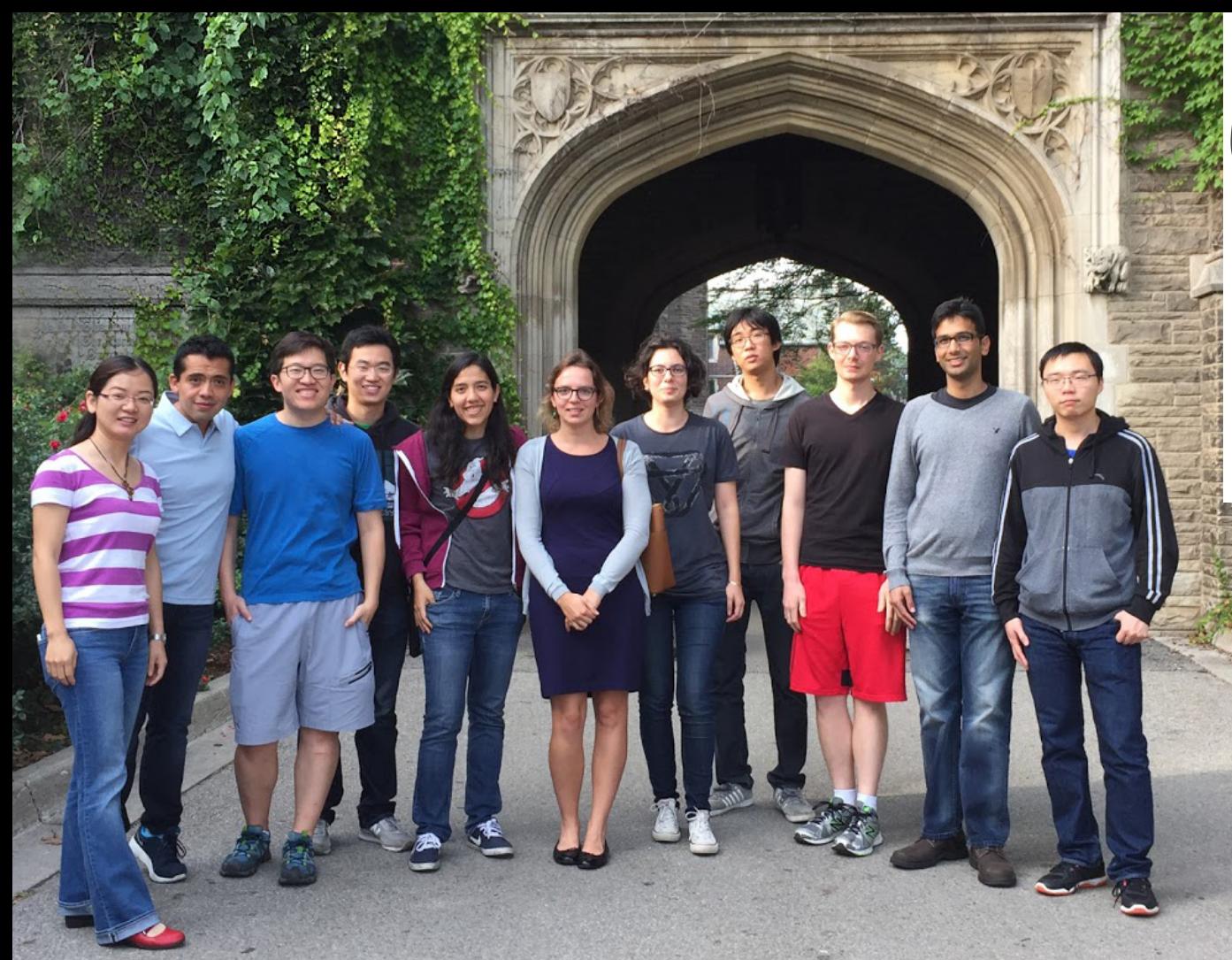
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It should always be borne in mind that when part is modified, so will be other parts, through certain dimly seen causes ... which lead to the many mysterious cases of correlation, which we do not in the least understand.

Charles Darwin

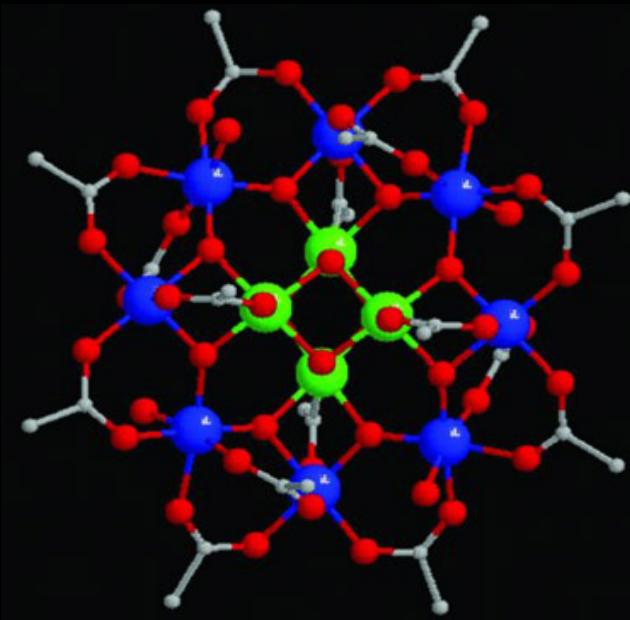
Operating \$: NSERC, FWO, Compute Canada,...

Fellowships: Banting, FWO, MITACS, NSERC, OGS, Steacie, Swiss NSF, Vanier,...



What Are We Trying to Do?

- Try to solve the electronic Schrödinger equation (especially for cases where existing methods work poorly).
- More-or-less exact results are already available for systems with less than about 50 electrons.
- To routinely treat systems with hundreds of electrons, one needs a method that is
 - mean-field.
 - size-consistent
 - no active spaces (black box)
- Example: Mn_{12} molecular magnet
 - $\sim 10^8$ thermally accessible states.
 - 752 electrons



The Orbital Paradigm

- Conventional approaches are based on the orbital picture.
- Key concepts:
 - Electron Cloud. Electrons do not interact directly; each electron feels the “average” effect of the cloud of the other electrons.
 - Mean-Field Hamiltonian. (Hartree-Fock, Kohn-Sham DFT, etc.)

$$\hat{H}_{\text{avg}} = \sum_{i=1}^{N_{\text{electrons}}} -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) + \overbrace{w(\mathbf{r}_i)}^{\text{average electron-electron potential of an electron at } \mathbf{r}_i}$$

- Slater determinant. Every orbital is either occupied or empty.

$$\begin{aligned} |\Psi_{\text{RHF}}\rangle &= a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger a_{2\uparrow}^\dagger a_{2\downarrow}^\dagger \cdots a_{P\uparrow}^\dagger a_{P\downarrow}^\dagger |\text{vacuum}\rangle & P = \frac{1}{2} N = \# \text{ of el. pairs} \\ &= a_1^\dagger a_{\bar{1}}^\dagger a_2^\dagger a_{\bar{2}}^\dagger \cdots a_P^\dagger a_{\bar{P}}^\dagger |\theta\rangle \end{aligned}$$

Use a Slater determinant as an initial guess; then correct from this starting point. **Linear combinations of Slater determinants.**

- Perturbation Theory (MP2, etc.)
- Random Phase Approximations (RPA)
- Configuration Interaction (Linear Combination of Sl. dets.)

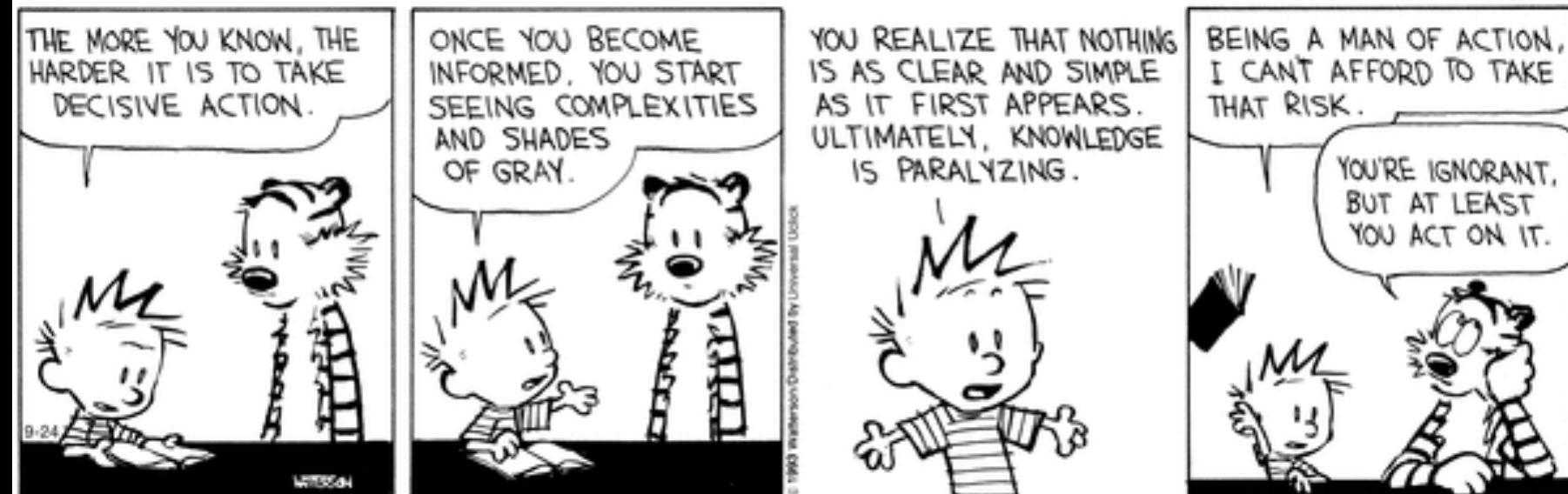
$$|\Psi_{\text{CISDT...}}\rangle = \left(\overbrace{1 + \sum_{\substack{i \leq N \\ a > N}} c_i^a a_a^\dagger a_i + \sum_{\substack{i,j \leq N \\ b,a > N}} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \sum_{\substack{i,j,k \leq N \\ a,b,c > N}} c_{ijk}^{abc} a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i}^{\text{CISD}} \right) |\Phi_{\text{HF}}\rangle$$

- Coupled Cluster Product Form.

$$|\Psi_{\text{CCSDT...}}\rangle = \left(\overbrace{\prod_{\substack{i \leq N \\ a > N}} (1 + t_i^a a_a^\dagger a_i) \prod_{\substack{i,j \leq N \\ a,b > N}} (1 + t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i) \prod_{\substack{i,j,k \leq N \\ a,b,c > N}} (1 + t_{ijk}^{abc} a_a^\dagger a_b^\dagger a_c^\dagger a_k a_j a_i) \cdots}^{\text{CCSD}} \right) |\Phi_{\text{HF}}\rangle$$

$$= \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots) |\Phi_{\text{HF}}\rangle$$

One dominant electron configuration \Rightarrow the product of spin-orbitals is a good starting point & standard methods work.
Many important electron configurations \Rightarrow the orbital picture is invalid...the problem of strong correlation...



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

A single electron configuration dominates in most:

- ✓ stable structures of organic molecules (organic thermochemistry & chemical equilibria)
 - but not transition-metal compounds, lanthanides, etc.
 - but not transition states. (kinetics)
- ✓ closed-shell inorganic molecules
 - but not open shells.
- ✓ for very weak electron interactions
- ✓ for very strong electron interactions (broken symmetry)
 - but not “intermediate” cases.
 - but not for attractive “effective” electron-electron interactions.

The orbital picture breaks down if:

- ...if there are many important electron configurations.
- ...if it impossible to assign “occupied” and “unoccupied” orbitals.
- ...if the electron-electron repulsion energy is similar to or greater than the splitting between frontier orbitals (orbitals near the Fermi level).

Examples: superconductors; quantum phase transitions; large quantum dots; large conjugated organic molecules; Wigner crystal; spin-frustrated systems; heavy fermion materials; molecular magnets; model Hamiltonians (Hubbard, PPP, Heisenberg, Richardson); d-block and f-block chemistry (esp. with noninnocent ligands)

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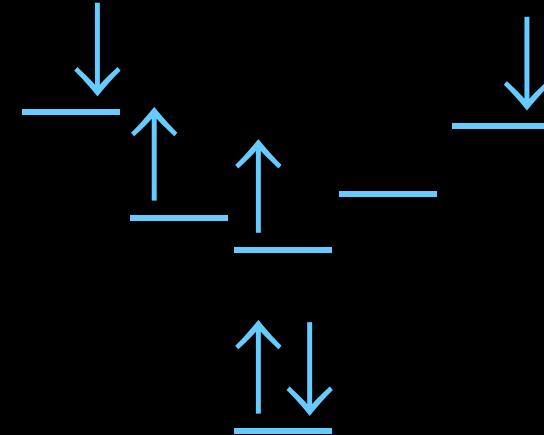
KS-DFT

MBPT n

CCSD...

AP*G

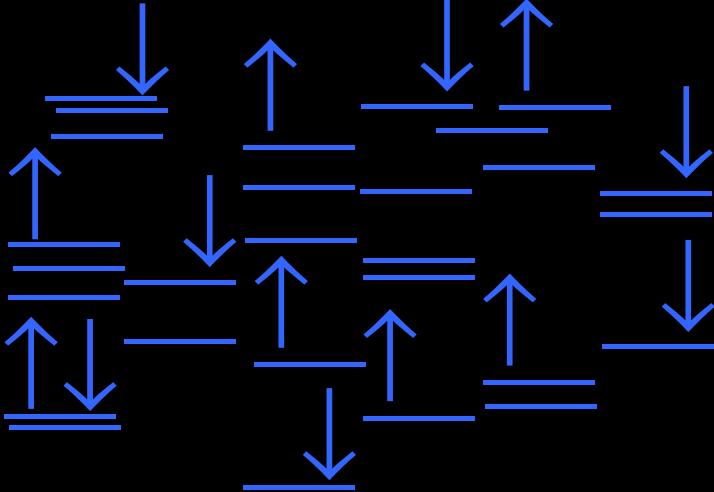
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CASSCF (<20)

DMRG (<50)

AP*G



AP*G

“Lewis” Picture of Electron Pair Configurations



The wavefunction for an electron pair looks like

$$G_p^\dagger |\text{vacuum}\rangle = \sum_{i,j=1}^{N_{\text{basis}}} c_{ij;p} a_j^\dagger a_i^\dagger |\text{vacuum}\rangle = \sum_{i,j=1}^{N_{\text{basis}}} c_{ij;p} |\phi_i \phi_j\rangle$$

The Antisymmetric Product of Geminals (APG)

$$|\Psi_{\text{APG}}\rangle = G_1^\dagger G_2^\dagger \cdots G_P^\dagger |\text{vacuum}\rangle$$

Hurley, Lennard-Jones, & Pople, Proc. R. Soc. London vA220, 446 (1953).

Parr, Ellison, & Lykos, J. Chem. Phys. v24, 1106 (1956).

Parks & Parr, J. Chem. Phys. v28, 335 (1958).

McWeeny (& Sutcliffe) Proc. Roy. Soc. London A253, 242 (1959); A273, 103 (1963).

Kutzelnigg J. Chem. Phys. v40, 3640 (1964).

Miller & Ruedenberg, J. Chem. Phys. v43, S88 (1965); v48, 3414 (1968).

Key advantage: Describes strong correlations.

Key disadvantage: *Very* expensive; $O(N!)$ computational cost.

Hurley, Lennard-Jones, & Pople, Proc. R. Soc. London vA220, 446 (1953).
Parr, Ellison, & Lykos, J. Chem. Phys. v24, 1106 (1956).
Parks & Parr, J. Chem. Phys. v28, 335 (1958).
E. Kapuy, Act. Phys. Hung. v9, 237 (1958), v10, 125 (1959), v11, 97 (1960), v12, 85 (1960).

McWeeny (& Sutcliffe) Proc. Roy. Soc. London A253, 242 (1959); A273, 103 (1963).
Kutzelnigg J. Chem. Phys. v40, 3640 (1964).
Miller & Ruedenberg, J. Chem. Phys. v43, S88 (1965); v48, 3414 (1968).
Levy, Stevens, Shull, & Hagstrom J. Chem. Phys. v52, 5483 (1970).
Paldus, Cizek, & Sengupta, J. Chem. Phys. v55, 2452 (1971); v57, 638 (1972); v57, 652 (1972).

Silver, J. Chem. Phys. v50, 5108 (1969).

Surjan, in Correlation and Localization, ed. P. R. Surjan (1999) Vol 203.
Surjan, Szabados, Jeszenszki, and Zoboki, J. Math. Chem. v50, 534 (2012).

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).

Use a unitary transformation to write the geminals in natural-orbital representation,

$$G_p^\dagger = \sum_{i,j}^{N_{\text{basis}}} c_{ij;p} a_j^\dagger a_i^\dagger \rightarrow \sum_i \tilde{c}_{i;p} \tilde{a}_{2i}^\dagger \tilde{a}_{2i-1}^\dagger = \sum_i \tilde{c}_{i;p} \tilde{a}_i^\dagger \tilde{a}_{\bar{i}}^\dagger$$

P-O. Lowdin, Phys. Rev. v97, 1474 (1955)

Antisymmetric Product of Interacting Geminals (APIG)

$$\begin{aligned} |\Psi_{\text{APIG}}\rangle &= G_1^\dagger(\tilde{c}_{i,1}) G_2^\dagger(\tilde{c}_{i,2}) \cdots G_P^\dagger(\tilde{c}_{i,P}) |\text{vacuum}\rangle \\ &= \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,1} a_i^\dagger a_{\bar{i}}^\dagger \right) \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,2} a_i^\dagger a_{\bar{i}}^\dagger \right) \cdots \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,1} a_i^\dagger a_{\bar{i}}^\dagger \right) |\text{vacuum}\rangle \end{aligned}$$

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

$$|\Psi_{\text{APIG}}\rangle = \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,1} a_i^\dagger a_{\bar{i}}^\dagger \right) \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,2} a_i^\dagger a_{\bar{i}}^\dagger \right) \cdots \left(\sum_{i=1}^{N_{\text{basis}}} \tilde{c}_{i,1} a_i^\dagger a_{\bar{i}}^\dagger \right) |\text{vacuum}\rangle$$

Consider the less abstract case of a polynomial

$$p(x_1, x_2, \dots, x_n) = \left(\sum_{i=1}^n c_{i,1} x_i \right) \left(\sum_{i=1}^n c_{i,2} x_i \right) \cdots \left(\sum_{i=1}^n c_{i,P} x_i \right)$$

or, to be explicit, for example,

$$\begin{aligned} p(x_1, x_2, x_3, x_4) &= \left(c_{1,1} \color{purple}{x}_1 + c_{2,1} x_2 + c_{3,1} \color{brown}{x}_3 + c_{4,1} \color{teal}{x}_4 \right) \\ &\quad \times \left(c_{1,2} \color{purple}{x}_1 + c_{2,2} x_2 + c_{3,2} \color{brown}{x}_3 + c_{4,2} \color{teal}{x}_4 \right) \\ &\quad \vdots \\ &\quad \times \left(c_{1,6} \color{purple}{x}_1 + c_{2,6} x_2 + c_{3,6} \color{brown}{x}_3 + c_{4,6} \color{teal}{x}_4 \right) \end{aligned}$$

$$\begin{pmatrix} c_{1,1}x_1 + c_{2,1}x_2 \\ +c_{3,1}x_3 + c_{4,1}x_4 \end{pmatrix} \begin{pmatrix} c_{1,2}x_1 + c_{2,2}x_2 \\ +c_{3,2}x_3 + c_{4,2}x_4 \end{pmatrix} \begin{pmatrix} c_{1,3}x_1 + c_{2,3}x_2 \\ +c_{3,3}x_3 + c_{4,4}x_4 \end{pmatrix} \dots \begin{pmatrix} c_{1,6}x_1 + c_{2,6}x_2 \\ +c_{3,6}x_3 + c_{4,6}x_4 \end{pmatrix}$$

The coefficient of a term in the expansion is given as the permanent of a matrix. E.g., the coefficient of $x_1x_3^2x_4^3$ is

$$\frac{1}{2!3!} \left| \begin{array}{cccccc} c_{1,1} & c_{1,2} & c_{1,3} & c_{1,4} & c_{1,5} & c_{1,6} \\ c_{2,1} & c_{2,2} & c_{2,3} & c_{2,4} & c_{2,5} & c_{2,6} \\ c_{2,1} & c_{2,2} & c_{2,3} & c_{2,4} & c_{2,5} & c_{2,6} \\ c_{4,1} & c_{4,2} & c_{4,3} & c_{4,4} & c_{4,5} & c_{4,6} \\ c_{4,1} & c_{4,2} & c_{4,3} & c_{4,4} & c_{4,5} & c_{4,6} \\ c_{4,1} & c_{4,2} & c_{4,3} & c_{4,4} & c_{4,5} & c_{4,6} \end{array} \right|^+$$

So the APIG wavefunction can be expanded in terms of (a factorial number of) Slater determinants,

$$\left| \Psi_{\text{APIG}} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} \left| \mathbf{C}(\mathbf{m}) \right|^+ \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

Hurley; Thesis (Trinity College, Cambridge, 1952)

Similar to all-pair (doubly-occupied) configuration interaction

$$\left| \Psi_{\text{DOCI}} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} c_{m_1 m_2 \cdots m_{N_{\text{basis}}}} \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

Weinhold & Wilson, J. Chem. Phys. v46, 2752 (1967).

Problem: permanents are very difficult to evaluate (#P hard)

Valiant, Theoretical Computer Science v8, 189 (1979).

Mathematics Trick

There are certain matrices whose permanents are easy to evaluate.

$$c_{i,p} = \frac{1}{w_i y_p - x_i z_p} \sim \frac{\zeta_i}{\varepsilon_i - \lambda_p}$$

then the permanent is a ratio of determinants,

$$\left[\begin{matrix} c_{i,p} \end{matrix} \right]^+ = \frac{\left[\begin{matrix} c_{i,p}^2 \end{matrix} \right]}{\left[\begin{matrix} c_{i,p} \end{matrix} \right]}$$

C.W. Borchardt, Crelle's Journal, 53, 193-198 (1855).

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

Physics Trick

Use the “weak” formulation of the eigenvalue problem;

$$\langle \Phi | \hat{H} | \Psi \rangle = E \langle \Phi | \Psi \rangle \quad \forall \Phi$$

We choose to project against just the pair excitations,

$$\langle \hat{H} \Phi_{\text{HF}} | \Psi \rangle = E \langle \Phi_{\text{HF}} | \Psi \rangle$$

$$\langle \hat{H} \Phi_{ii}^{a\bar{a}} | \Psi \rangle = E \langle \Phi_{ii}^{a\bar{a}} | \Psi \rangle$$

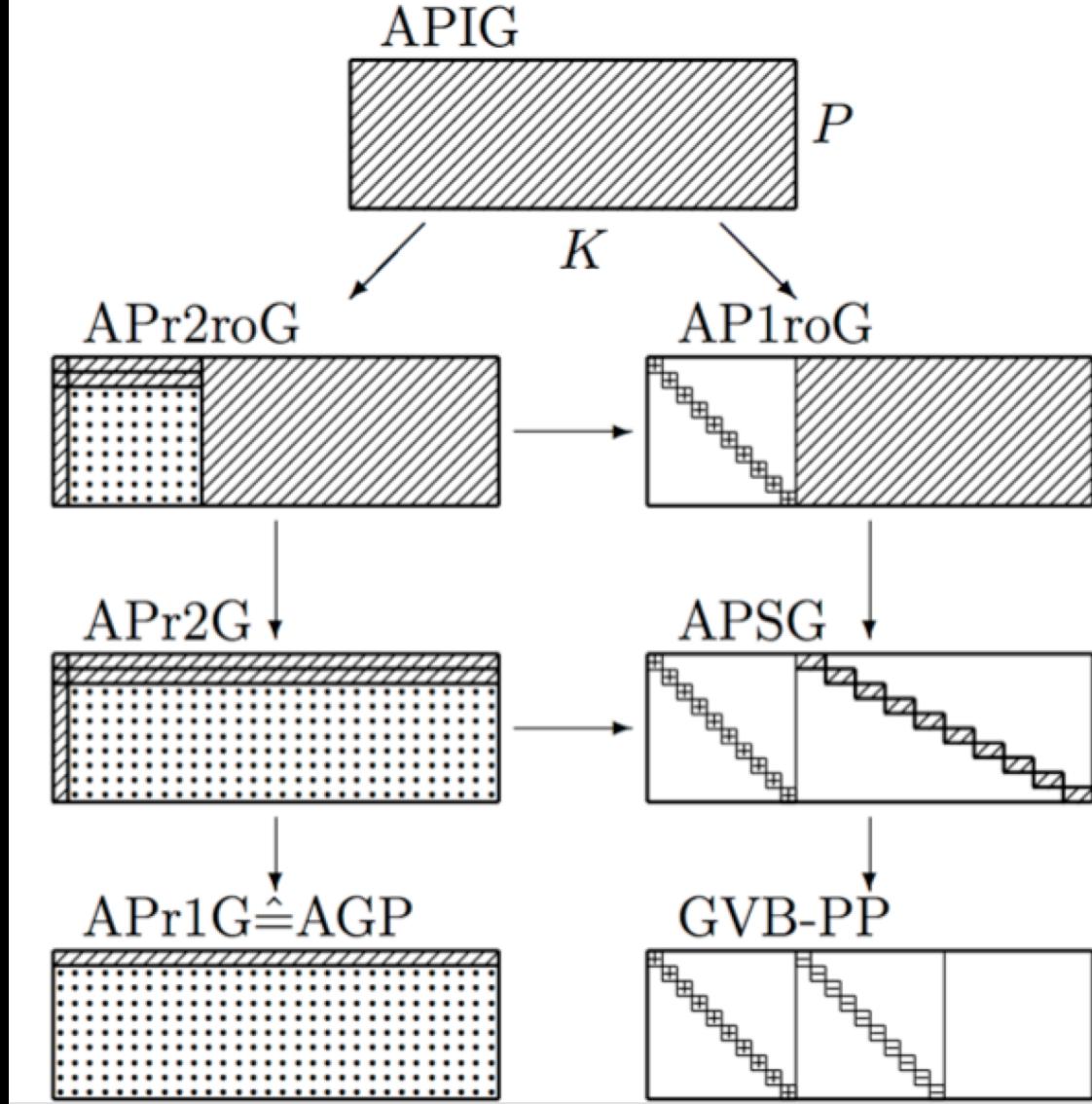
With this choice, there are other efficient geminal forms that can be used too.

Limacher, Ayers, Johnson, De Baerdemacker, Van Neck, and Bultinck, J. Chem. Theory Comp. v9, 1394 ('13). Limacher et al. Mol. Phys. v112, 853 ('14); Boguslawski et al. Phys. Rev. B v89, 201106 ('14); Boguslawski et al. J. Chem. Phys. v140, 214114 ('14).

$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} c_{p,i} a_i^\dagger a_{\bar{i}}^\dagger$$

$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} \left(\frac{\zeta_i}{\varepsilon_i - \lambda_p} \right) a_i^\dagger a_{\bar{i}}^\dagger$$

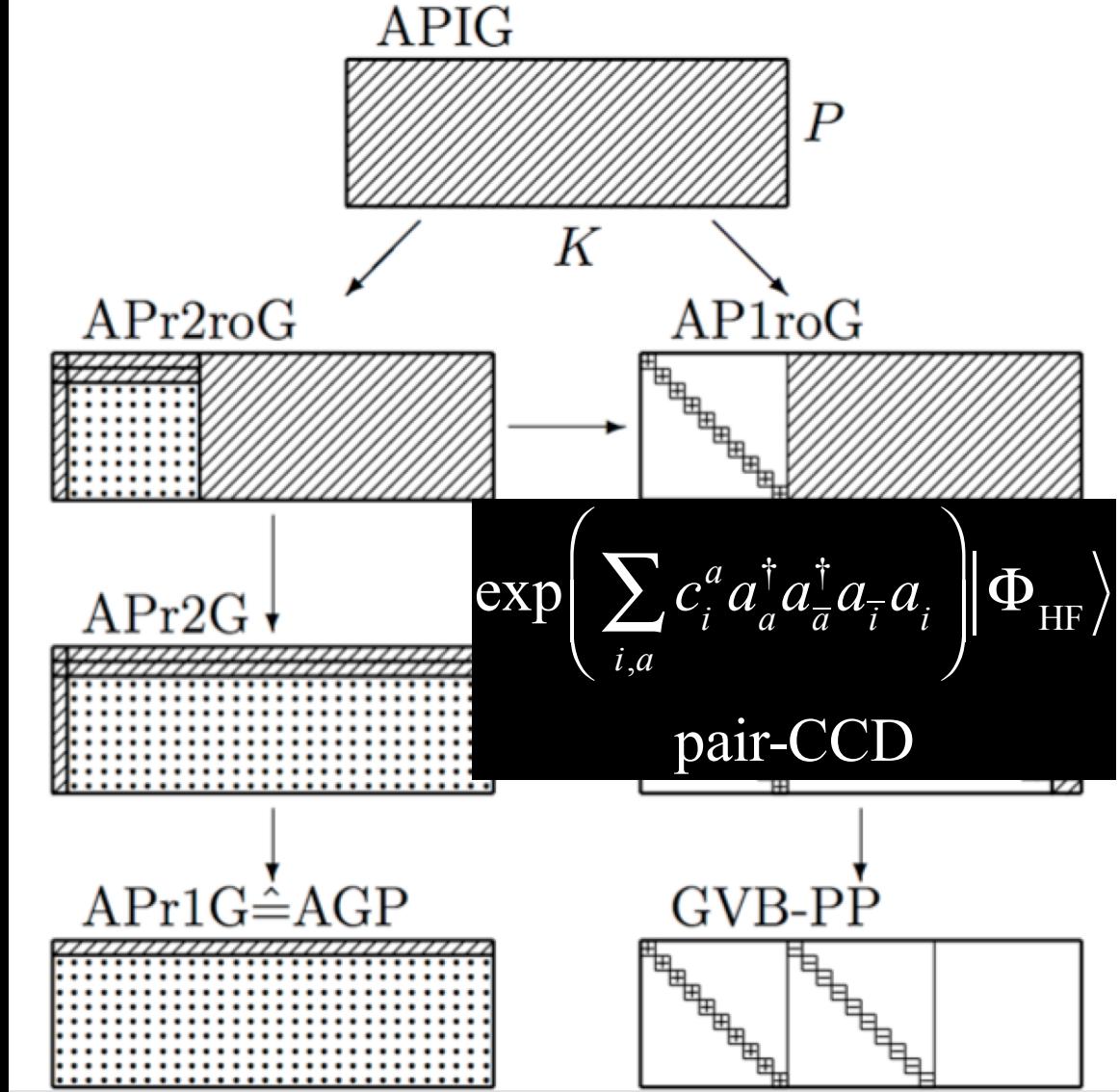
$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} \zeta_i a_i^\dagger a_{\bar{i}}^\dagger$$



$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} c_{p,i} a_i^\dagger a_{\bar{i}}^\dagger$$

$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} \left(\frac{\zeta_i}{\varepsilon_i - \lambda_p} \right) a_i^\dagger a_{\bar{i}}^\dagger$$

$$\prod_{p=1}^P \sum_{i=1}^{N_{\text{basis}}} \zeta_i a_i^\dagger a_{\bar{i}}^\dagger$$



Results for AP1roG

(Correlation energies in milliHartree)

System	Basis	R (a.u.)	DOCI	AP1roG	%E _c
Ne	6-31G	—	-43.382		37.4%
CH ₄	6-31G	2.05311	-75.953		63.0%
(H ₂) ₅	STO-6G	2.0/2.5	-162.208		86.7%
(H ₂) ₅	STO-6G	2.0/3.0	-182.020		94.4%
(H ₂) ₅	STO-6G	2.0/4.0	-195.507		98.9%

$$\left| \Psi_{AP^*G} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} \left| \mathbf{C}(\mathbf{m}) \right|^+ \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

$$\left| \Psi_{\text{DOCI}} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} c_{m_1 m_2 \cdots m_{N_{\text{basis}}}} \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

Results for AP1roG

(Correlation energies in milliHartree)

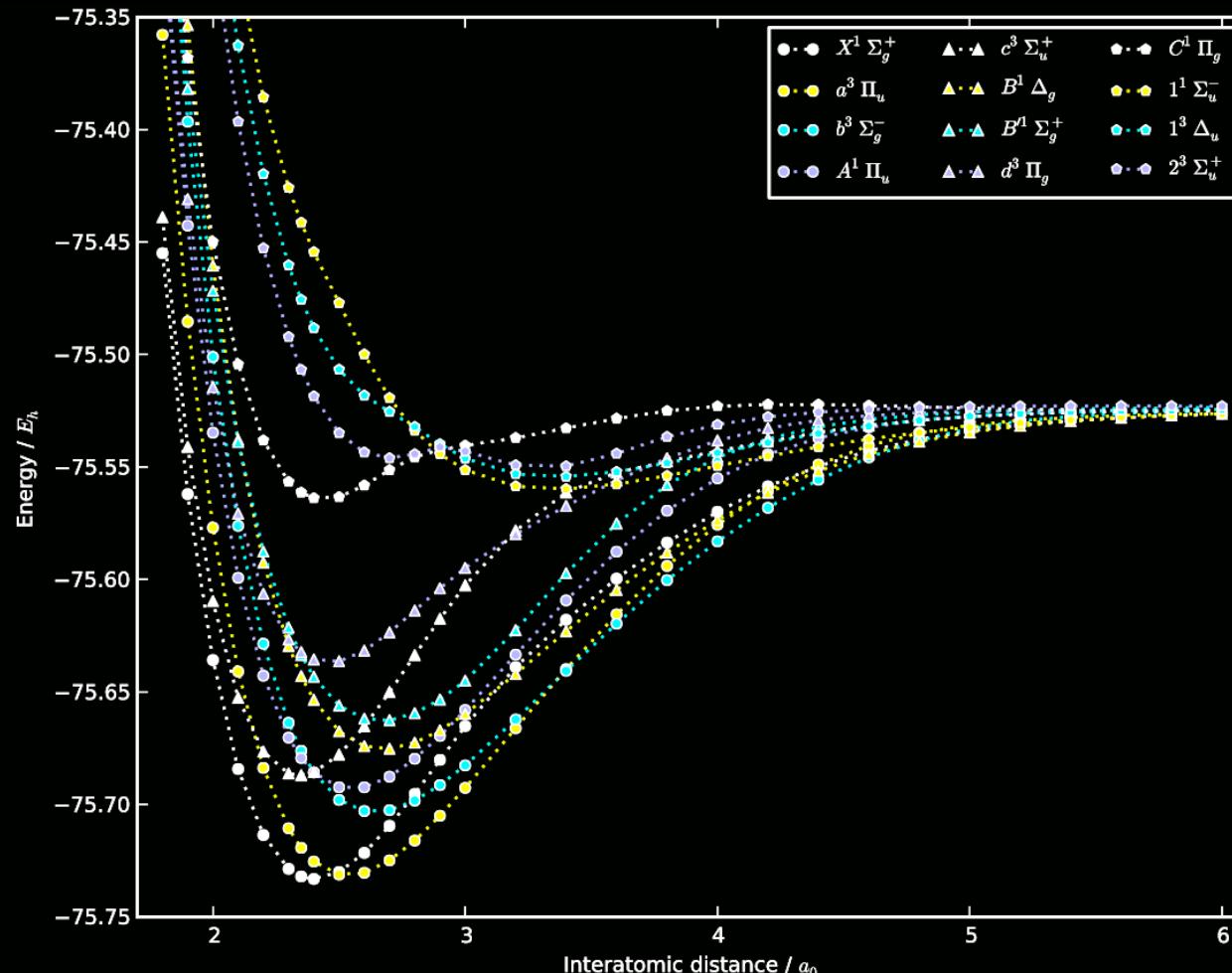
System	Basis	R (a.u.)	DOCI	AP1roG	%E _c
Ne	6-31G	—	-43.382	-43.384	37.4%
CH ₄	6-31G	2.05311	-75.953	-75.946	63.0%
(H ₂) ₅	STO-6G	2.0/2.5	-162.208	-162.273	86.7%
(H ₂) ₅	STO-6G	2.0/3.0	-182.020	-182.083	94.4%
(H ₂) ₅	STO-6G	2.0/4.0	-195.507	-195.535	98.9%

$$\left| \Psi_{\text{AP}^*\text{G}} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} \left| \mathbf{C}(\mathbf{m}) \right|^+ \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

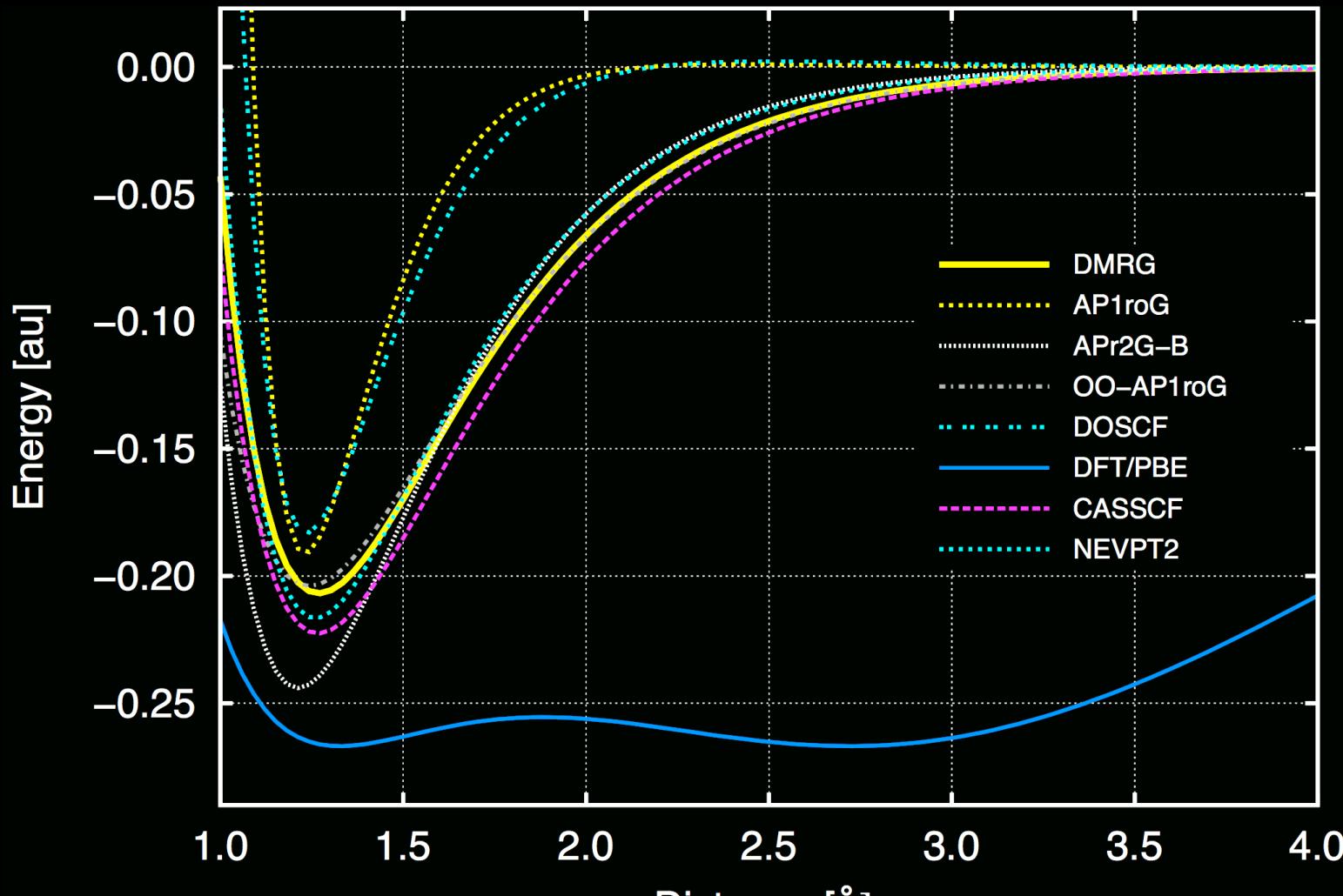
$$\left| \Psi_{\text{DOCI}} \right\rangle = \sum_{\left\{ m_i \in \{0,1\} \middle| \sum_{i=1}^{N_{\text{basis}}} m_k = \frac{N}{2} \right\}} c_{m_1 m_2 \cdots m_{N_{\text{basis}}}} \left(a_1^\dagger a_1^\dagger \right)^{m_1} \left(a_2^\dagger a_2^\dagger \right)^{m_2} \cdots \left(a_{N_{\text{basis}}}^\dagger a_{N_{\text{basis}}}^\dagger \right)^{m_{N_{\text{basis}}}} \left| \theta \right\rangle$$

Example: Carbon Dimer (C_2). Hard because *lots* of low-lying states.

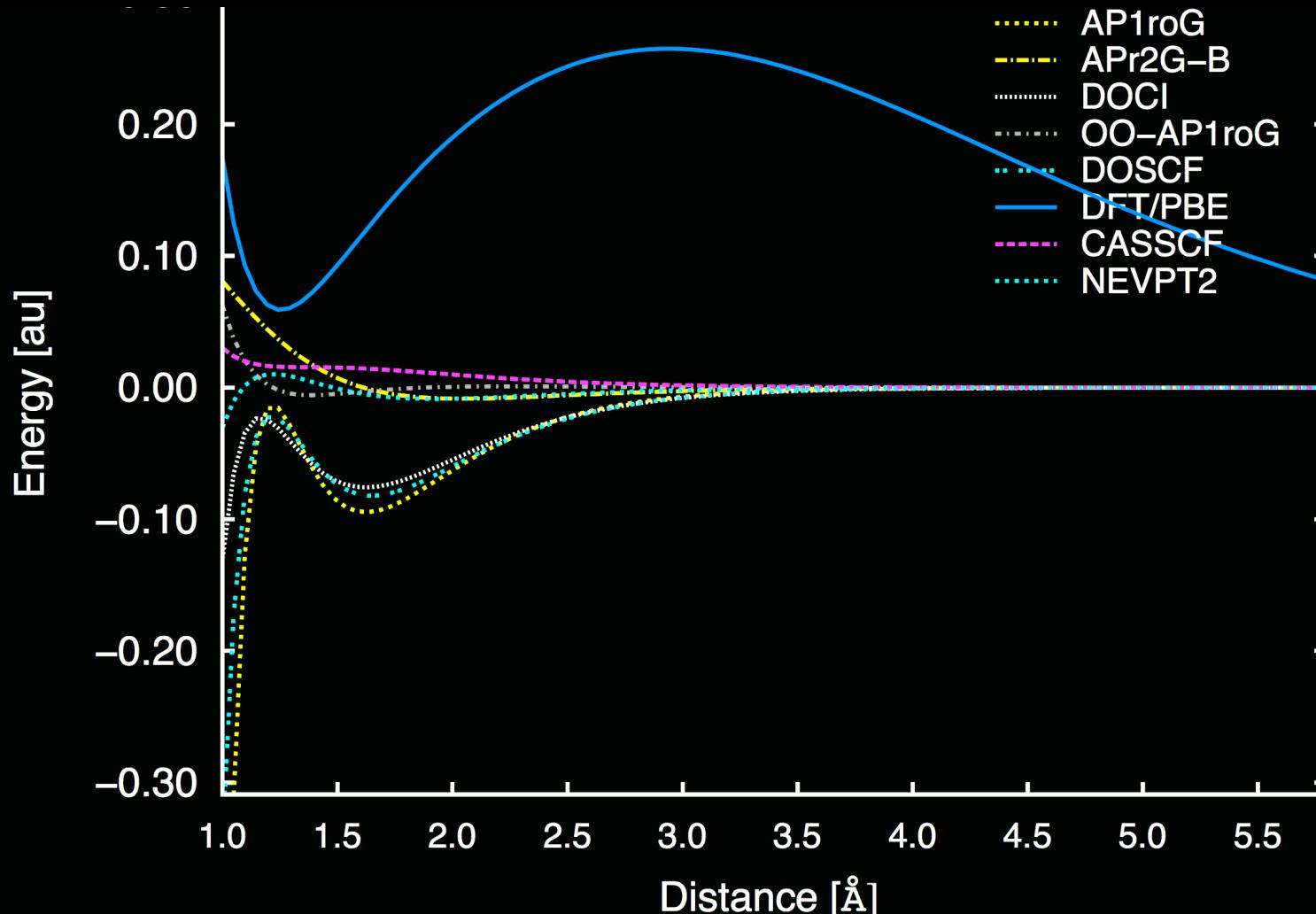
Wouters, Poelman, Ayers, Van Neck Comp. Phys. Comm. v185, 1501 (2014).



Energy of C_2 (cc-pVDZ)



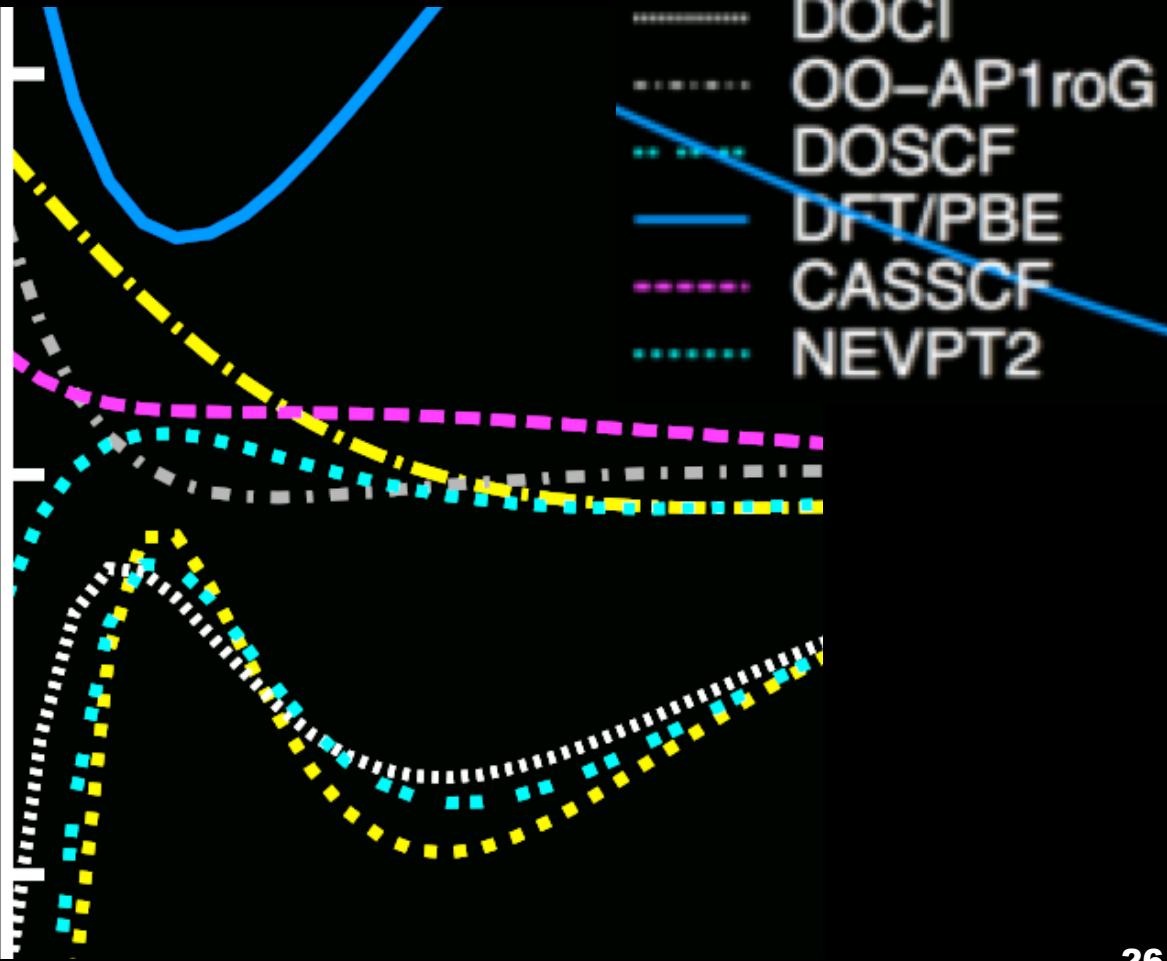
Error in Energy of C₂ (cc-pVDZ)



Error in Energy of C_2 (cc-pVDZ)

Energy [au]

0.10
0.00
-0.10



Orbital Optimization

Analogous to Orbital-Optimized Coupled Cluster (vOO-AP^{*}G)
(Minimize energy subject to the constraint that the projected-Schrödinger equation holds)

$$\min_{\{U_{mn}\}} E_{\text{AP1roG}}(U_{mn})$$
$$\left\{ U_{mn} \middle| \langle \Phi_{ii}^{a\bar{a}} | \hat{H} | \Psi_{\text{AP1roG}}(c_{i,a}) \rangle = E \langle \Phi_{ii}^{a\bar{a}} | \Psi_{\text{AP1roG}}(c_{i,a}) \rangle \right\}$$

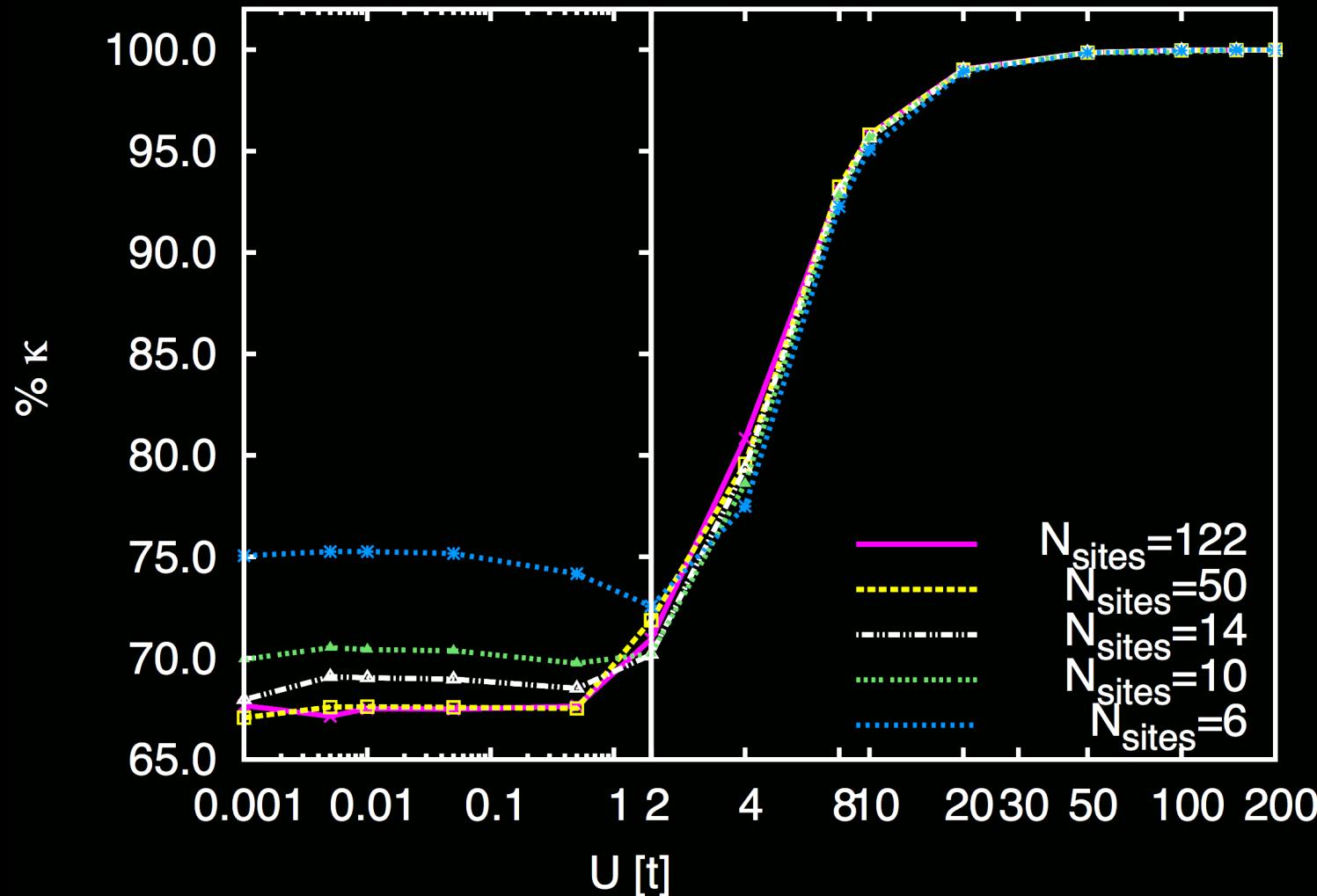
Limacher, Kim, Ayers, Johnson, De Baerdemacker, Van Neck, Bultinck, Mol. Phys. v112, 853 (2014).

Boguslawski, Tecmer, Ayers, Bultinck, De Baerdemacker, Van Neck, Phys. Rev. B v89, 201106 (2014).

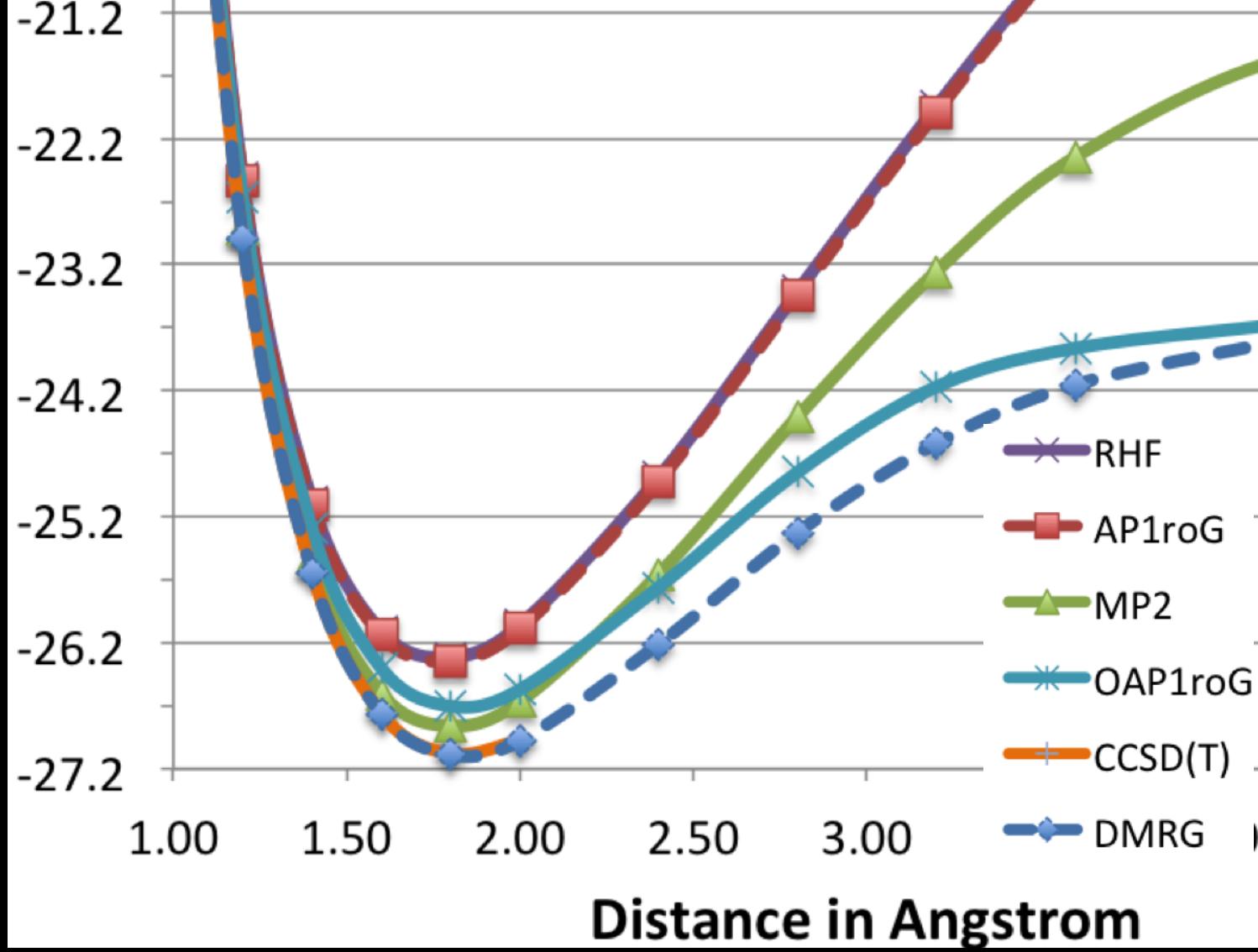
Stein, Henderson, Scuseria, J. Chem. Phys. v140, 214113 (2014).

Boguslawski, Tecmer, Limacher, Johnson, Ayers, Bultinck, De Baerdemacker, Van Neck, D., J. Chem. Phys. v140, 214114 (2014).

% of Correlation Energy in Hubbard Model (oo-AP1roG)



H_{50} Symmetric Stretch



Problem: Dynamical correlation is missing!

Multi-Configuration Perturbation Theory:

Kobayashi, Szabados, Nakai, Surjan, J. Chem. Th. Comp. v6, 2024 (2010).

Limacher, Ayers, Johnson, De Baerdemacker, Van Neck, Bultinck, PCCP v16, 5061 (2014).

Linearized Coupled-Cluster (CEPA-like)

Zoboki, Szabados, Surjan, J. Chem. Theory Comp. v9, 2602 (2013).

K. Boguslawski & P. W. Ayers, J. Chem. Theory Comp. (accepted).

Pawel Tecmer poster IV-20.

Extended Random Phase Approximation

Pastorczak, Pernal, PCCP v17, 8622 (2015).

frozen-pair CCSD

Henderson, Bulik, Stein, Scuseria, J. Chem. Phys. v141, 244104 (2014).

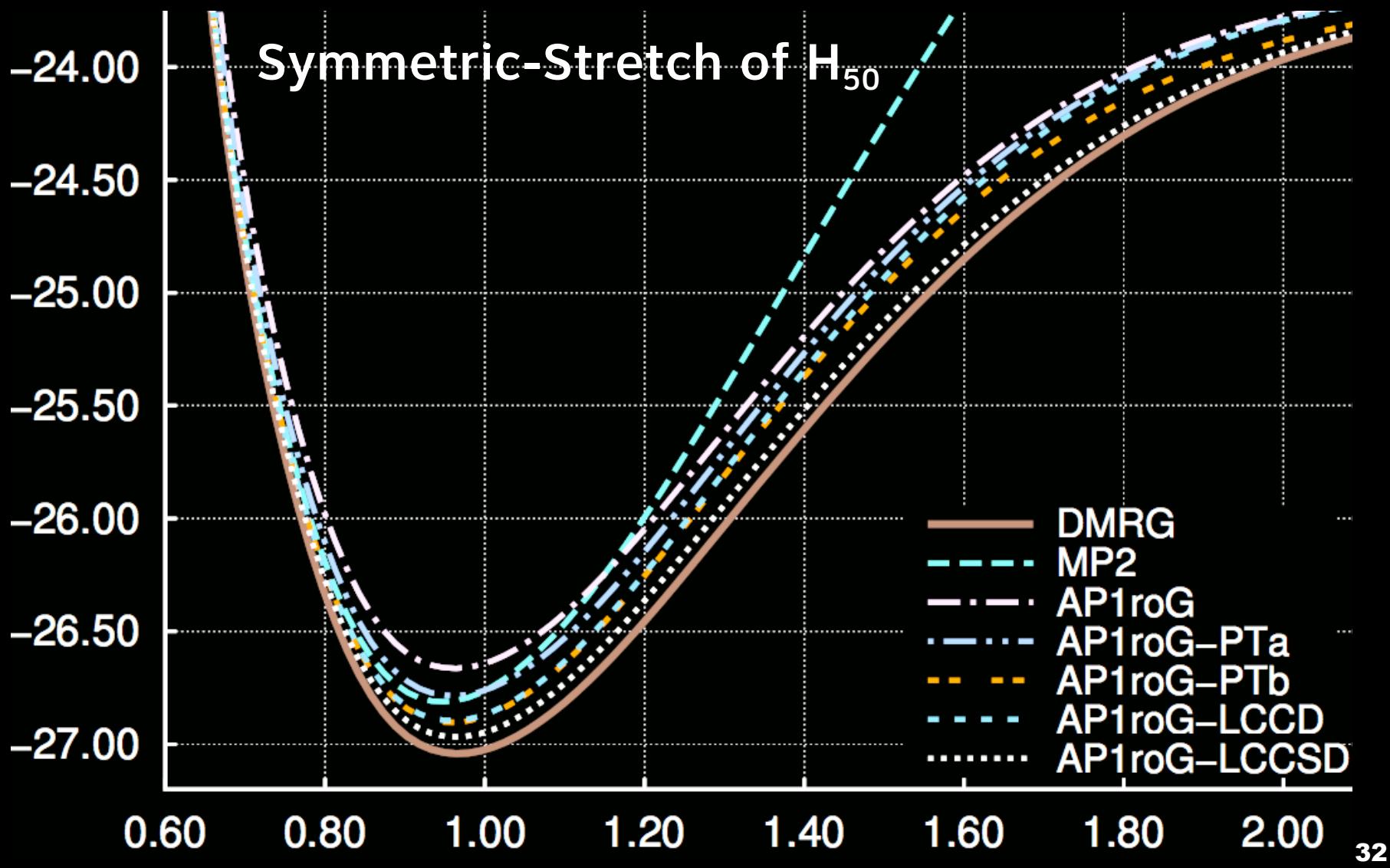
- (1) Write perturbation expansions; (2) project on $|\tilde{\Psi}\rangle$;
 (3) Expand in Slater determinants.

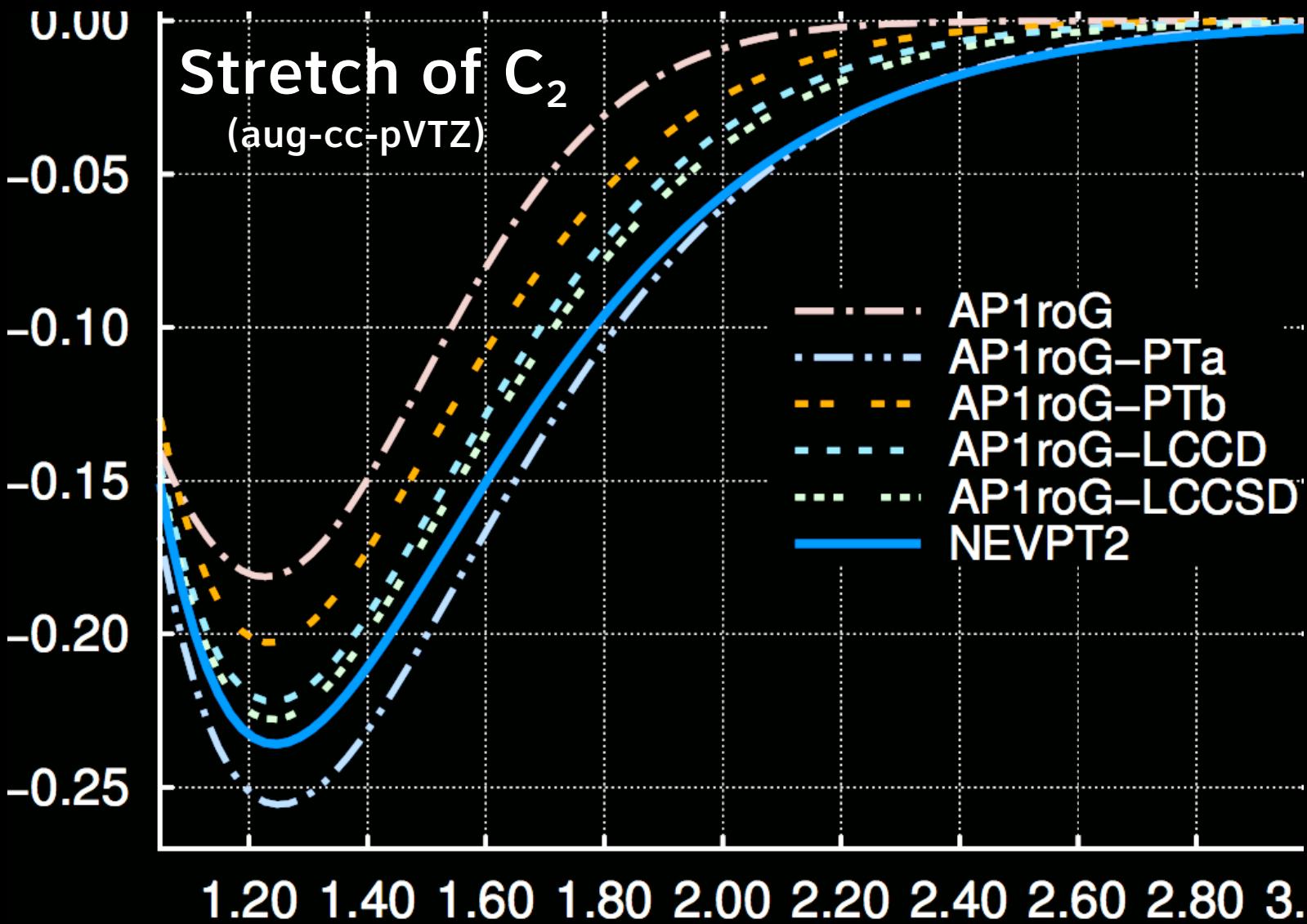
$$\hat{H}^{(0)} = E^{(0)} + \frac{|\Psi^{(0)}\rangle\langle\tilde{\Psi}|}{\langle\tilde{\Psi}|\Psi^{(0)}\rangle} + \hat{P}\hat{V}\hat{P}$$

$$\hat{P} = 1 - \frac{|\Psi^{(0)}\rangle\langle\tilde{\Psi}|}{\langle\tilde{\Psi}|\Psi^{(0)}\rangle}$$

PTA: $\hat{V} = \hat{F}$ $|\tilde{\Psi}\rangle = |\Phi_0\rangle$

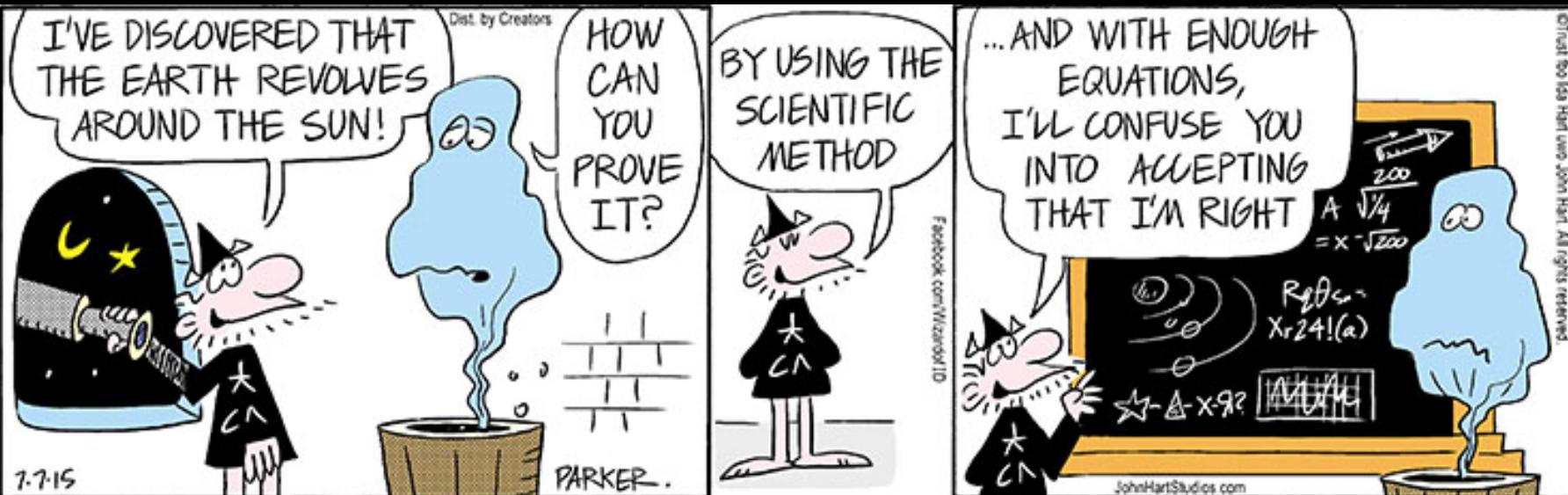
PTB: $\hat{V} = \frac{\hat{F}}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle}$ $|\tilde{\Psi}\rangle = |\Psi^{(0)}\rangle$





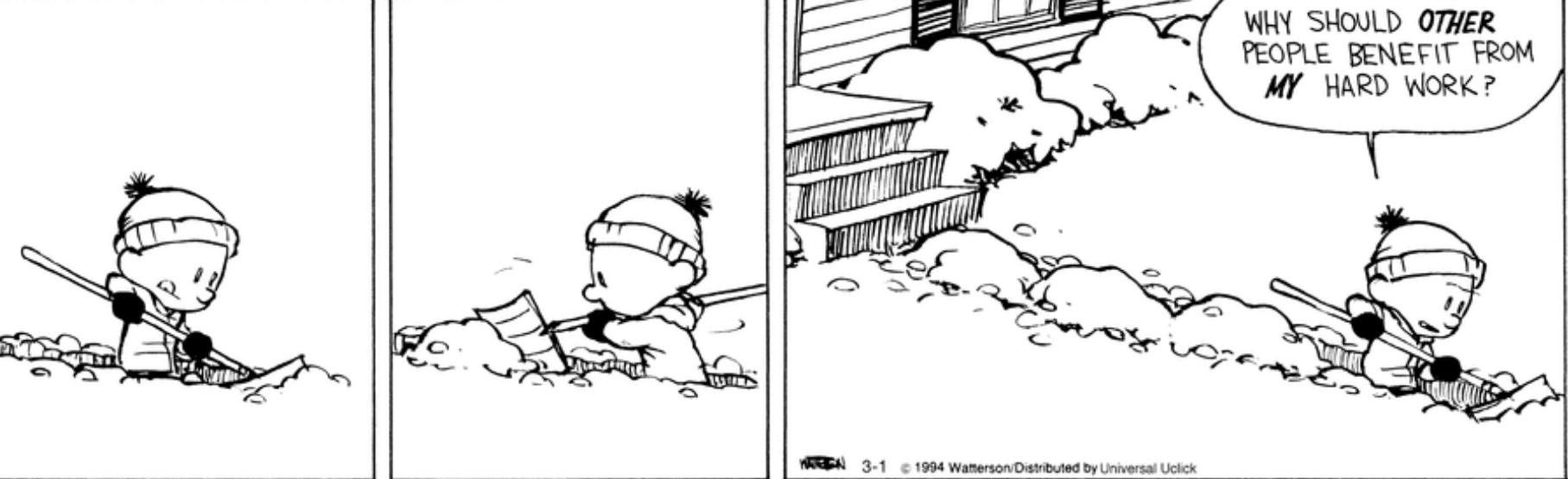
Extensions

- Variational approaches
- Open Shells



Conclusions

- The geminal product form captures most strong correlation effects. It is a mean-field method for pairs, and thus very fast. (It is applicable for hundreds, even thousands, of electrons.)
- Key Idea: Build your wavefunction from electron pair quasiparticles (geminals), not quasi-independent electrons. Related to (extended) coupled-cluster pairs.
- 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.
- Limitation: We need to find better ways to include dynamic correlation.
- Limitation: We need to find extensions that effectively address open-shell states (unpaired electrons).



<http://theochem.github.io/horton>

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