A brief introduction to coupled cluster methods for electronic structure theory

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Outline

- Motivation and Basics
- Coupled cluster Ansatz
- Basis and system size convergence
- Applications: Solids, Molecules on Surfaces, Defects
- Conclusion

Ab-initio calculations of many-electron systems

KS-DFT versus traditional QC wavefunction theories

$$H = -\sum_{i=1}^{N} \frac{\hbar^{2}}{2m_{e}} \Delta_{\mathbf{r}_{i}} - \sum_{i=1}^{N} V_{N}(\mathbf{r}_{i}) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} |\Psi\rangle \approx (1 + C) |\Psi_{0}\rangle$$
Approximate wavefunction
$$H\Psi = E\Psi$$
Kohn-Sham theory using approximate xc
$$\left\{ -\frac{\hbar^{2}}{2m} \nabla^{2} + V(\vec{r}) + e^{2} \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^{3}r + \mu_{xc}[n(\vec{r})] \right\} \phi_{i}(\vec{r}) = \varepsilon_{i} \phi_{i}(\vec{r})$$

Why CC theory?

Error of atomization enthalpies in kJ/mol

	ΔE	PBE	SCAN	$\operatorname{CCSD}(T)$
	N2	-65.04	35.41	0.47
	H2	20.51	7.79	0.00
	F2	-58.41	-1.46	2.11
	O2	-96.94	-28.38	2.39
	CO	-39.38	26.48	-0.06
	C2H2	-40.12	16.69	-0.80
2	$\rm COH$	-46.58	-0.03	2.84
	CO2	-15.49	-25.29	0.12
	CC 2	-109.58	-4.93	-0.38
	L 12O2	-55.08	13.15	0.58
C N	H2O	-5.03	19.28	0.02
2 0	HCO	-67.33	-9.42	0.41
De ·	HF	-1.59	14.94	0.05
	NO	-82.85	6.60	1.53
	OH	-11.08	-4.56	0.35
	HNO	-74.63	25.14	1.09
	CN	-69.55	13.10	6.57
	HCN	-55.09	24.25	-0.17
	CF	-51.94	-10.92	0.40
	NH2	-25.49	-9.97	0.54
	NH	-22.63	-11.15	0.51
	rms	56.5	17.5	1.8

Energy



Ea

Ζ



Ground & Excited States, Gradients, Response properties, ...

Hierarchical methods and Jacob's ladder

Systematic improvability





Wavefunction methods: HF



The Hartree-Fock approximation $|\Psi\rangle \approx |\Phi_0\rangle$

Single Slater determinant

$$\Phi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Orbital optimization

Constraint minimization

$$\min_{\{\chi_a\}} \left\{ E_{\rm HF}[\{\chi_a\}] - \sum_a^{\rm occ} \varepsilon_a \langle \chi_a | \chi_a \rangle \right\}$$

Eigenvalue equation for effective one-body problem

$$f(\mathbf{x})\chi_i(\mathbf{x}) = \varepsilon_i \chi_i(\mathbf{x})$$

Energy expectation value

$$E_{\rm HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_a^{\rm occ} h_{aa} + \frac{1}{2} \sum_{a,b}^{\rm occ} \langle ab | | ab \rangle$$

One-body operators

$$h_{aa} = \int \mathrm{d}\mathbf{x} \; \chi_a^*(\mathbf{x}) h(\mathbf{r}) \chi_a(\mathbf{x})$$

Two-body operators $\langle ij|kl \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \frac{\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}$

HF approximation

- Correct antisymmetry of **wavefunction**
- Cubic scaling of comp. complexity wrt. N
- Self-interaction free and exact for 1 electron
- By definition no electronic correlation

$$E_{\rm c} = E_0 - E_{\rm HF}$$

Wavefunction methods: Full Cl



The exact wavefunction

CI expansion



=> Compact approximations to CI vector are needed!

Wavefunction methods: CCSD



A compact approximation to the many-electron wave function

 $|\Psi\rangle = e^{\hat{T}}|\Psi_0\rangle$ F. Coester and H. Kümmel (1950s) Jiři Čížek (1966)

Applications of CC theories to periodic systems:

Arponen, Bishop, Freeman, ...

Stoll, Paulus, Sauer, Schwerdtfeger, Manby, Chan, Berkelbach, Schütz, Usvyat, Hirata, ...

> Rodney J. Bartlett and Monika Musiał Rev. Mod. Phys. 79, 291 (2007)

A compact approximation to the many-electron wave function

$$|\Psi\rangle = e^{\hat{T}}|\Psi_0\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$
 CCS, CCSD, ...



Rodney J. Bartlett and Monika Musiał Rev. Mod. Phys. 79, 291 (2007)

A compact approximation to the many-electron wave function

$$\begin{split} |\Psi\rangle &= e^{\hat{T}} |\Psi_0\rangle \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots \quad \text{CCS, CCSD, } \dots \\ \hat{T}_1 &= \sum_i^{\text{occ. virt.}} \sum_a^{\text{virt.}} t_i^a a_a^{\dagger} a_i \qquad \hat{T}_2 = \frac{1}{4} \sum_{ij}^{\text{occ. virt.}} \sum_{ab}^{\text{virt.}} t_{ij}^{ab} a_a^{\dagger} a_i a_b^{\dagger} a_j \end{split}$$

Recall algebra for creation and annihilation operators from second quantization for general states p and q

$$\begin{bmatrix} \hat{a}_{p}^{\dagger}, \hat{a}_{q}^{\dagger} \end{bmatrix}_{+} = 0; \quad \begin{bmatrix} \hat{a}_{p}, \hat{a}_{q} \end{bmatrix}_{+} = 0; \quad \begin{bmatrix} \hat{a}_{p}, \hat{a}_{q}^{\dagger} \end{bmatrix}_{+} = \delta_{pq}$$

Energy:
$$\langle \Psi_0 | e^{-\hat{T}} H e^{\hat{T}} | \Psi_0 \rangle$$

Ab initio Hamiltonian in second quantization is given by

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^{\dagger} \hat{a}_q + \frac{1}{4} \sum_{pqrs} g_{pqrs} \hat{a}_p^{\dagger} \hat{a}_q^{\dagger} \hat{a}_r \hat{a}_s$$

CC theory employs a similarity transformed H

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$$

Hausdorff expansion for H containing 2-electron operators yields

$$\bar{H} = \hat{H} + \left[\hat{H}, \hat{T}\right] + \frac{1}{2!} \left[\left[\hat{H}, \hat{T}\right], \hat{T} \right] + \frac{1}{3!} \left[\left[\left[\hat{H}, \hat{T}\right], \hat{T} \right], \hat{T} \right] + \frac{1}{4!} \left[\left[\left[\left[\hat{H}, \hat{T}\right], \hat{T} \right], \hat{T} \right], \hat{T} \right], \hat{T} \right]$$

$\begin{array}{l} Coupled \ Cluster \ Theory \\ \bar{\mathit{H}} = \hat{\mathit{H}} + \left[\hat{\mathit{H}}, \hat{\mathit{T}}\right] + \frac{1}{2!} \left[\left[\hat{\mathit{H}}, \hat{\mathit{T}}\right], \hat{\mathit{T}} \right] + \frac{1}{3!} \left[\left[\left[\hat{\mathit{H}}, \hat{\mathit{T}}\right], \hat{\mathit{T}} \right], \hat{\mathit{T}} \right] + \frac{1}{4!} \left[\left[\left[\left[\hat{\mathit{H}}, \hat{\mathit{T}}\right], \hat{\mathit{T}} \right], \hat{\mathit{T}} \right], \hat{\mathit{T}} \right], \hat{\mathit{T}} \right] \end{array}$

 \bar{H} contains a string of operators

To compute $\langle \Psi_0 | e^{-\hat{T}} H e^{\hat{T}} | \Psi_0 \rangle$ we need to evaluate action of operators on bra- and ket-state.

Example: $E_{CC} = \langle 0 | \bar{H} | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | \hat{H}\hat{T} | 0 \rangle$ because $\langle 0 | \hat{a}_a^{\dagger} \hat{a}_i = 0$ and \hat{H} deexcites two electrons at most $\langle 0 | \hat{H} | 0 \rangle = E_{HF}$ $\langle 0 | \hat{H}\hat{T} | 0 \rangle = \langle 0 | \hat{H} \left(\hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) | 0 \rangle = E_{corr.}$

Energy:
$$\langle \Psi_0 | e^{-\hat{T}} H e^{\hat{T}} | \Psi_0 \rangle = E_{\text{HF}} + E_{\text{corr.}}$$

$$E_{\rm C} = \sum_{ij}^{\rm occ. \ unocc.} \left(\frac{1}{2} t^a_i t^b_j + \frac{1}{4} t^{ab}_{ij} \right) \langle ij || ab \rangle = \bigcup + \bigcup + \text{Singles}$$

$$\underbrace{ \left\langle ij | ab \right\rangle }_{ = t^{ab}_{ij} }$$

Amplitudes: $\langle \Psi_{\mu} | e^{-\hat{T}} H e^{\hat{T}} | \Psi_{0} \rangle = 0$

$$\mu = 1 \to t_i^a$$
$$\mu = 2 \to t_{ij}^{ab}$$

Example: CCD Amplitudes ($\hat{T} = \hat{T}_2$)

$$\begin{split} t^{ab}_{ij} &= \frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} (\langle ij||ab \rangle + \langle cj||kb \rangle t^{ac}_{ik} + \langle ci||ka \rangle t^{bc}_{jk} + \langle cd||kl \rangle t^{db}_{lj} t^{ac}_{ik} \\ &+ \frac{1}{2} \langle cd||ab \rangle t^{cd}_{ij} + \frac{1}{2} \langle ij||kl \rangle t^{ab}_{kl} + \frac{1}{4} \langle cd||kl \rangle t^{cd}_{ij} t^{ab}_{kl} \\ &- \langle cj||ka \rangle t^{bc}_{ik} - \langle ci||kb \rangle t^{ac}_{jk} - \langle cd||kl \rangle t^{da}_{lj} t^{bc}_{ik} \\ &+ \frac{1}{2} \langle cd||kl \rangle \left[t^{ab}_{lj} t^{cd}_{ik} - t^{ab}_{li} t^{cd}_{jk} + t^{db}_{ij} t^{ac}_{kl} - t^{da}_{ij} t^{bc}_{kl} \right]) \end{split}$$





Rev. Mod. Phys. 79, 291 (2007)

Why use CCSD in solids?



Exact 2-electron Wavefunction

CC theory for excited states

Charge-neutral excitation can be computed using the EOM approach

$$\hat{Q}\hat{H}\hat{R} |\Psi_{\rm CC}\rangle = \hat{Q}\hat{H}\hat{R}e^{\hat{T}} |0\rangle = E_R \hat{Q}\hat{R} |\Psi_{\rm CC}\rangle$$
where
$$\hat{Q} = \sum_{a,i} \left| \substack{a \\ i} \right\rangle \left\langle \substack{a \\ i} \right| + \frac{1}{4} \sum_{a,b,i,j} \left| \substack{ab \\ ij} \right\rangle \left\langle \substack{ab \\ ij} \right|$$

• The following state-specific vector represents the excited state wrt the CC wavefunction (here at the level of CCSD)

$$\hat{R} = r_0 + \sum_{a,i} r_i^a \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4} \sum_{a,b,i,j} r_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i, \qquad r_\mu \in \mathbb{C}$$

• Rewriting the equation yields an "equation-of-motion"

$$\left[\hat{Q}\bar{H},\hat{R}\right]\left|0\right\rangle=\Delta E_{R}\hat{Q}\hat{R}\left|0\right\rangle$$

Extending this to Fock-space yields quasi-particle energies (EOM-IP/EA)

J. F. Stanton and R. J. Bartlett, The Journal of Chemical Physics 98, 7029 (1993)

Challenges for CC calculations

Computer implementation of equations (hundreds of terms)

 $0 = v_{ak_{a}bk_{b}}^{ik_{i}jk_{j}*} + \sum_{k,l} \sum_{k_{k}} \chi_{ik_{i}jk_{j}}^{kk_{k}lk_{l}} t_{kk_{k}lk_{l}}^{ak_{a}bk_{b}} + \sum_{k,l} \chi_{ik_{i}jk_{j}}^{kk_{k}lk_{l}} t_{kk_{k}}^{ak_{a}bk_{b}} + \sum_{c,d} \sum_{k_{c}} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}} + \sum_{c,d} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}} + P\sum_{c} \lambda_{ck_{c}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}bk_{b}} + \sum_{c,d} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}} + \sum_{c,d} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}} + P\sum_{c} \lambda_{ck_{c}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}bk_{b}} + \sum_{c,d} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}} + P\sum_{c} \lambda_{ck_{c}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}bk_{b}} + \sum_{c,d} \chi_{ck_{c}dk_{d}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}} + P\sum_{c} \lambda_{ck_{c}}^{ak_{a}bk_{b}} t_{ik_{i}jk_{j}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}k_{k}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{a}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{k}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{i}bk_{b}} t_{ik_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{i}k_{k}}^{ak_{i}bk_{b}} t_{ik_{i}k_{i}}^{ck_{c}bk_{b}} + \sum_{c} \chi_{ik_{i}k_{k$

 $+P\sum_{k,c}\sum_{k_{k}}(2\chi_{ik_{i}ck_{c}}^{ak_{a}kk_{k}}-\chi_{ck_{c}ik_{i}}^{ak_{a}kk_{k}})t_{kk_{k}jk_{j}}^{ck_{c}bk_{b}}-P\sum_{k,c}\sum_{k_{k}}\chi_{ik_{i}ck_{c}}^{ak_{a}kk_{k}}t_{kk_{k}jk_{j}}^{bk_{b}ck_{c}}-P\sum_{k,c}\sum_{k_{k}}\chi_{ck_{c}ik_{i}}^{bk_{b}kk_{k}}t_{kk_{k}jk_{j}}^{ak_{a}ck_{c}},$

- Scaling of computational complexity w.r.t.
 - #electrons
 - #virtual orbitals
 - #auxiliary basis functions

Quantum Chemistry methods



Methods

Comp. parameters, e.g. #grid points, basis set ...

Computational bottle necks in periodic coupled cluster calculations

Convergence of cohesive energy of carbon diamond w.r.t. system size







Computational complexity of CCSD

Computational bottle necks in periodic coupled cluster calculations

Convergence of cohesive energy of carbon diamond w.r.t. system size







- Scaling of computational complexity w.r.t. number of
 - virtual orbitals -> (OSVs, NOs, F12)
 - basis functions -> (Low rank approximations)
 - electrons -> (Local approximations, finite size corr.)

Applications: Phase diagrams of solids

Phase diagrams of C and BN

Low-density (Graphitic) vs. high-density (Diamond)





T. Gruber and A. Grüneis, PRB 98, 134108 (2018)

Phase diagrams of C and BN



T. Gruber and A. Grüneis, PRB 98, 134108 (2018)

Applications: Molecules on surfaces





Good agreement between CC and DMC

Y. S. Al-Hamdani, M. Rossi, D. Alfè, T. Tsatsoulis, B. Ramberger, J. G. Brandenburg, A. Zen, G. Kresse, A. Grüneis, A. Tkatchenko and A. Michaelides, JCP 147, 044710 (2017)

Water on Graphene

$E_{ m ad}/ m meV$	Method	Comment		
-130	DFT/CC	Corrects DFT based on differ- ences on small clusters		
-130	DFT-SAPT	Extrapolation from cluster		
-70 ± 10^{b}	DMC	Periodic system, large stochas- tic error, finite-size effects		
-135	i-CCSD(T)	Incremental expansion, correla- tion from cluster, small basis set		
-87	p-CCSD(T) ^a	Periodic system, finite-size cor- rected		
-99 ± 6^b	DMC ^a	Periodic system, finite-size cor- rected		









J. G. Brandenburg, A. Zen, M. Fitzner, B. Ramberger, G. Kresse, T. Tsatsoulis, A. Grüneis, A. Michaelides, D. Alfè, JPCL 10, 358 (2019) Applications: Defects in solids

Excited states in F centers





4.95

5.4

4.48

4.71

5.20

3.4

G₀W₀@LDA0-BSE⁴⁰

 $G_0 W_0 @LDA0^{40}$

 $G_0 W_0 @PBE^{41}$

GW0@PBE41

GW@PBE41

A. Gallo et. al. J. Ch	em. Phys. 154,	064106 (2021)
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Final Remarks

- Traditional QC methods such as MP2 and CC theory ...
 - become more widely-used for materials science
 - achieve high accuracy and can serve as useful benchmark methods
- Open challenges include
 - overcoming the computational complexity bottle necks
 - treatment of strong correlation in solids using CC-related techniques

Acknowledgements





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