A brief introduction to coupled cluster methods

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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

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r + \mu_{xc}[n(\vec{r})] \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

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Why CC theory?

Error of atomization enthalpies in kJ/mol

ΔE	PBE	SCAN	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
CCH	-46.58	-0.03	2.84
CH2	-15.49	-25.29	0.12
CO2	-109.58	-4.93	-0.38
H2O2	-55.08	13.15	0.58
H2O	-5.03	19.28	0.02
HCO	-67.33	-9.42	0.41
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

Chemical accuracy 4.184 kJ/mol

$$H\Psi = E\Psi$$

Ground & Excited States, Gradients, Response properties, …

Hierarchical methods and Jacob's ladder

Systematic improvability

Approximate xc

Approximate wavefunctions

Full CI (Exact)

CCSD(T)

CCSD

MP2

HF

Accuracy

PRB 134, 024116 (2011)

Wavefunction methods: HF

The Hartree-Fock approximation

$$|\Psi\rangle \approx |\Phi_0\rangle$$

Single Slater determinant

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

Energy expectation value

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

One-body operators $h_{aa} = \int \mathrm{d}\mathbf{x}\, \chi_a^*(\mathbf{x}) h(\mathbf{r}) \chi_a(\mathbf{x})$

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

Orbital optimization

Constraint minimization

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

↓

Eigenvalue equation for effective one-body problem

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

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**

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

Wavefunction methods: Full CI

The exact wavefunction

CI expansion

The CI expansion

$$|\Psi_{\mathrm{CI}}\rangle = c_0|\Phi_0\rangle + \sum_a^{\mathrm{occ}}\sum_r^{\mathrm{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\mathrm{occ}}\sum_{r<s}^{\mathrm{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \cdots$$

$$\text{Number of SDs} = \frac{M!}{N!(M-N)!}$$

Determining the CI vectors

Variational method leads to linear algebra problem to determine coefficients

$$\begin{pmatrix} \langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_a^r\rangle & \langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_a^r \\ c_{ab}^{rs} \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_0 \\ c_a^r \\ c_{ab}^{rs} \\ \vdots \end{pmatrix}$$

Due to presence of at most two-body operators in *H* the above matrix becomes sparse

However, Hamiltonian-Matrix is of size:

$$\frac{M!}{N!(M-N)!} \times \frac{M!}{N!(M-N)!}$$

=> **Compact approximations** to CI vector are needed!

Wavefunction methods: CCSD

Coupled Cluster Theory

A compact approximation to the many-electron wave function

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

F. Coester and H. Kümmel (1950s)

Jiří 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)

Coupled Cluster Theory

A compact approximation to the many-electron wave function

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

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

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CCS, CCSD, …

$$\hat{T}_1 = \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} t_i^a a_a^\dagger a_i \qquad \hat{T}_2 = \frac{1}{4} \sum_{ij}^{\text{occ.}} \sum_{ab}^{\text{virt.}} t_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j$$

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

$$\left[\hat{a}_p^\dagger, \hat{a}_q^\dagger\right]_+ = 0; \quad [\hat{a}_p, \hat{a}_q]_+ = 0; \quad \left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \delta_{pq}$$

Coupled Cluster Theory

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

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

Coupled Cluster Theory

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

$\bar{H}$ 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:

$$E_{\mathrm{CC}} = \langle 0 | \bar{H} | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | \hat{H}\hat{T} | 0 \rangle$$

because $\langle 0 | \hat{a}_a^\dagger \hat{a}_i = 0$ and $\hat{H}$ deexcites two electrons at most

$$\langle 0 | \hat{H} | 0 \rangle = E_{\mathrm{HF}}$$

$$\langle 0 | \hat{H}\hat{T} | 0 \rangle = \langle 0 | \hat{H} \left(\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1{}^2 \right) | 0 \rangle = E_{\mathrm{corr.}}$$

Coupled Cluster Theory

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

$$E_{\mathrm{C}} = \sum_{ij}^{\mathrm{occ.}} \sum_{ab}^{\mathrm{unocc.}} \left(\frac{1}{2} t_i^a t_j^b + \frac{1}{4} t_{ij}^{ab} \right) \langle ij || ab \rangle =$$

+ Singles

$$= \langle ij | ab \rangle$$

$$= t_{ij}^{ab}$$

Coupled Cluster Theory

Amplitudes: $\langle \Psi_\mu | e^{-\hat{T}} H e^{\hat{T}} | \Psi_0 \rangle = 0$

$$\mu = 1 \rightarrow t_i^a$$

$$\mu = 2 \rightarrow t_{ij}^{ab}$$

$$\ldots$$

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

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

Coupled Cluster Theory

$\hat{T}_2$ Amplitude Equations (t_{ij}^{ab})

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$\hat{T}_2$ Amplitude Equations (t_{ij}^{ab})

1st

$E_c^{\mathrm{MP2}} =$

2nd

Coupled Cluster Theory

$\hat{T}_2$ Amplitude Equations (t_{ij}^{ab})

1st

2nd

3rd

The QC hierarchy

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

MP2 theory

$$\hat{T} = \hat{T}_2$$

- Exact to 2nd-order PT

O(N^5)

CCSD theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

- Exact to 3rd-order PT
- ph-RPA, pp-RPA, hh-RPA
- Exact for 2e systems

O(N^6)

CCSD(T) theory

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$$

$\hat{T}_3$ in perturbative manner

- "Chemical Accuracy"
- Exact for 2e systems

O(N^7)

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

Why use CCSD in solids?

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

$E_{\mathrm{C}} =$ + Singles

$= \langle ij | ab \rangle$

$= t_{ij}^{ab}$

$\hat{T}_2$ Amplitude Equations (t_{ij}^{ab})

High-density limit in UEG

Antisymmetry

Low-density limit in UEG

Exact 2-electron Wavefunction

CC theory for excited states

- Charge-neutral excitation can be computed using the EOM approach

$$\hat{Q}\hat{H}\hat{R}\,|\Psi_{\mathrm{CC}}\rangle = \hat{Q}\hat{H}\hat{R}e^{\hat{T}}\,|0\rangle = E_R\hat{Q}\hat{R}\,|\Psi_{\mathrm{CC}}\rangle$$

where $\hat{Q} = \sum_{a,i} \left|\begin{matrix} a \\ i \end{matrix}\right\rangle\left\langle\begin{matrix} a \\ i \end{matrix}\right| + \frac{1}{4}\sum_{a,b,i,j} \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle\left\langle\begin{matrix} ab \\ ij \end{matrix}\right|$

- 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“

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

- 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)

$$
\begin{aligned}
0 = {} & v_{ak_a bk_b}^{ik_i jk_j *} + \sum_{k,l} \sum_{k_k} \chi_{ik_i jk_j}^{kk_k lk_l} t_{kk_k lk_l}^{ak_a bk_b} + \sum_{k,l} \chi_{ik_i jk_j}^{kk_k lk_l} t_{kk_k}^{ak_a} t_{lk_l}^{bk_b} + \sum_{c,d} \sum_{k_c} \chi_{ck_c dk_d}^{ak_a bk_b} t_{ik_i jk_j}^{ck_c dk_d} + \sum_{c,d} \chi_{ck_c dk_d}^{ak_a bk_b} t_{ik_i}^{ck_c} t_{jk_j}^{dk_d} + P \sum_{c} \lambda_{ck_c}^{ak_a} t_{ik_i jk_j}^{ck_c bk_b} \\
& - P \sum_{k} \lambda_{ik_i}^{kk_k} t_{kk_k jk_j}^{ak_a bk_b} + P \sum_{c} \left(v_{ik_i ck_c}^{ak_a bk_b} - \sum_{k} v_{ik_i ck_c}^{kk_k bk_b} t_{kk_k}^{ak_a} \right) t_{jk_j}^{ck_c} - P \sum_{k} \left(v_{ik_i jk_j}^{ak_a kk_k} + \sum_{c} v_{ik_i ck_c}^{ak_a kk_k} t_{jk_j}^{ck_c} \right) t_{kk_k}^{bk_b} \\
& + P \sum_{k,c} \sum_{k_k} (2\chi_{ik_i ck_c}^{ak_a kk_k} - \chi_{ck_c ik_i}^{ak_a kk_k}) t_{kk_k jk_j}^{ck_c bk_b} - P \sum_{k,c} \sum_{k_k} \chi_{ik_i ck_c}^{ak_a kk_k} t_{kk_k jk_j}^{bk_b ck_c} - P \sum_{k,c} \sum_{k_k} \chi_{ck_c ik_i}^{bk_b kk_k} t_{kk_k jk_j}^{ak_a ck_c},
\end{aligned}
$$

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

Cc4s: An open CC code

https://manuals.cc4s.org/

Quantum Chemistry 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 bottle necks in periodic coupled cluster calculations

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

Convergence of energy (UEG) w.r.t. basis set

Computational bottle necks in periodic coupled cluster calculations

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

$O(N^6)$

Convergence of energy (UEG) w.r.t. basis set

$O(n^2M^4)$

Computational complexity of CCSD

Computational bottle necks in periodic coupled cluster calculations

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

Convergence of energy (UEG) w.r.t. basis set

- 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)

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**

Water on *h*-BN

- 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_{ad}/meV	Method	Comment
-130	DFT/CC	Corrects DFT based on differences on small clusters
-130	DFT-SAPT	Extrapolation from cluster
-70 ± 10[b]	DMC	Periodic system, large stochastic error, finite-size effects
-135	i-CCSD(T)	Incremental expansion, correlation from cluster, small basis set
-87	p-CCSD(T) [a]	Periodic system, finite-size corrected
-99 ± 6[b]	DMC [a]	Periodic system, finite-size corrected

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

System	Method	Absorption	Emission
MgO	EE-EOM-CCSD	5.28	3.66
	Expt.[62]	5.0	2.4
	QMC[42]	5.0(1)	3.8(1)
	CASPT2[30]	5.44	4.09
	G_0W_0@LDA0-BSE[40]	4.95	3.4
	G_0W_0@LDA0[40]	5.4	
	G_0W_0@PBE[41]	4.48	
	GW_0@PBE[41]	4.71	
	GW@PBE[41]	5.20	

A. Gallo et. al. J. Chem. Phys. 154, 064106 (2021)

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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Thank you!

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