Multiconfigurational methods: past, present and the road ahead



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Content of the lectures

- Concepts
- Past
 - CASCI
 - MCSCF/CASSCF

MR Dynamical Correlation Approaches

• Density Matrix Renormalisation Group

Road ahead: Beyond "classical quantum chemistry"

Quantum Chemistry on Quantum Computers



- Present: "Sample" CI coefficients using an advanced optimisation algorithm



from H_2 ...

First example: Things to learn

Concepts





A quick reminder on Cl

$$|\Psi| = \sum C_{\zeta} |\Phi_{\zeta}|$$

- Orbital coefficients are fixed
- The parameters are chosen to minimise the energy
- Leads to eigenvalue problem Hc = Ec with $(H)_{\zeta_n} = \langle \phi_{\zeta} | \hat{H} | \phi_n \rangle$
- If all determinants $\{\phi\}$ of a given basis are included, we solve the Schrödinger equation projected onto the basis -> full CI (FCI)



Expand wave function as a linear combination of Slater determinants





A quick reminder on RHF

- Minimize the energy of one Slater determinant or a symmetry/spinadapted combination (CSFs) of Slater determinants
- Individual unoccupied orbitals have a limited meaning (HOMO/LUMO —> Koopman's theorem)

RHF wave function of H₂

$\Phi^{RHF}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g, \alpha}(x_1) \varphi_{1\sigma_g, \beta}(x_2) - \varphi_{1\sigma_g, \alpha}(x_2) \varphi_{1\sigma_g, \beta}(x_1) \right)$





 $= \varphi_{1\sigma_{g}}(\mathbf{r}_{1})\varphi_{1\sigma_{g}}(\mathbf{r}_{2}) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_{1}\sigma_{g}}\delta_{\sigma_{2}\beta} - \delta_{\sigma_{2}\sigma_{g}}\delta_{\sigma_{1}\beta}\right)$

 $\delta_{\sigma_1\alpha} = |\alpha\rangle \langle \sigma_1 | \alpha \rangle$

 $\Psi(x) = \sum_{x_i} |x_i\rangle \langle \Psi|x_i\rangle = \sum_{x_i} x_i \langle \Psi|x_i\rangle$

RHF wave function of H₂

$$\Phi^{RHF}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_g, \alpha} \right)$$
$$= \varphi_{1\sigma_g}(r_1)\varphi$$





 $(x_1)\varphi_{1\sigma_g,\beta}(x_2) - \varphi_{1\sigma_g,\alpha}(x_2)\varphi_{1\sigma_g,\beta}(x_1)\Big)$

 $\varphi_{1\sigma_{g}}(\mathbf{r}_{2}) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_{1}\alpha} \delta_{\sigma_{2}\beta} - \delta_{\sigma_{2}\alpha} \delta_{\sigma_{1}\beta} \right)$

RHF wave function of stretched H₂ in a minimal basis

 $S_A(\mathbf{r})$

Η



$$S_B(\mathbf{r})$$

Bonding orbital

.

$$\frac{1}{2}\left(\mathbf{s}_{A}(\mathbf{r}) + \mathbf{s}_{B}(\mathbf{r})\right)$$

$$\frac{1}{\sqrt{2}}(\mathbf{r}_{2}) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_{1} \alpha} \delta_{\sigma_{2} \beta} - \delta_{\sigma_{2} \alpha} \delta_{\sigma_{1} \beta} \right)$$

RHF wave function of stretched H₂ in a minimal basis



 $\frac{1}{2} \left(s_A(r_1) s_B(r_2) + s_A(r_2) s_B(r_1) + s_A(r_1) s_A(r_2) + s_B(r_1) s_B(r_2) \right)$

$$\frac{1}{\sqrt{2}} \left(r_2 \right) \times \frac{1}{\sqrt{2}} \left(\delta_{\sigma_1 \alpha} \delta_{\sigma_2 \beta} - \delta_{\sigma_2 \alpha} \delta_{\sigma_1 \beta} \right)$$

-0.75 FCI HF -0.8 MP2 -0.85 -0.9 Energy (a.u.) -0.95 -1 -1.05 -1.1 -1.15 -1.2 2 3 4



-0.75 FCI HF -0.8 MP2 -0.85 -0.9 Energy (a.u.) -0.95 -1 -1.05 -1.1 -1.15 -1.2 2 3 4







Near-degeneracies give rise to static correlation!



Near-degeneracies give rise to static correlation! Better ansatz?



Bonding orbital

$$\varphi_{1\sigma_{g}}(\mathbf{r}) = \frac{1}{\sqrt{2}} \left(\mathbf{S}_{A}(\mathbf{r}) + \mathbf{S}_{B}(\mathbf{r}) \right)$$



Anti-Bonding orbital

 $\varphi_{1\sigma_{u}}(\mathbf{r}) = \frac{1}{\sqrt{2}} \left(\boldsymbol{S}_{A}(\mathbf{r}) - \boldsymbol{S}_{B}(\mathbf{r}) \right)$







$$\begin{bmatrix} \left| \left(1\sigma_g \right)^2 \right\rangle - \left| \left(1\sigma_u \right)^2 \right\rangle \end{bmatrix}$$
$$\left(\varphi_{1\sigma_g}(\mathbf{r}_1) \varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1) \varphi_{1\sigma_u}(\mathbf{r}_2) \right)$$



$$\left|\Psi\right\rangle \equiv \frac{1}{\sqrt{2}} \left(\varphi_{1\sigma_{g}}(\mathbf{r}_{1})\varphi_{1\sigma_{g}}(\mathbf{r}_{2}) - \varphi_{1\sigma_{u}}(\mathbf{r}_{1})\varphi_{1\sigma_{u}}(\mathbf{r}_{2})\right)$$

 $\varphi_{1\sigma}$

$$S_g(\mathbf{r}) = \frac{1}{\sqrt{2}} \left(\frac{s_A(\mathbf{r}) + s_B(\mathbf{r})}{\sqrt{2}} \right)$$



$$\left(\varphi_{1\sigma_g}(\boldsymbol{r}_1)\varphi_{1\sigma_g}(\boldsymbol{r}_2)-\boldsymbol{\varphi_{1\sigma_u}}(\boldsymbol{r}_1)\boldsymbol{\varphi_{1\sigma_u}}(\boldsymbol{r}_2)\right)$$

 $= \frac{1}{\sqrt{2}} \left(\frac{s_A(r_1)s_B(r_2) + s_A(r_2)s_B(r_1)}{H \cdots H} \right)$ H \cdots H \cdots H \cdots H





The Past ...







Virtual spin-orbitals "secondary"

L active spin orbitals



Virtual spin-orbitals "secondary"

L active spin orbitals -> active orbitals



Virtual spin-orbitals "secondary"

CASCI is FCI in the active space!

L active spin orbitals —> active orbitals





Virtual spin-orbitals "secondary"

CASCI is FCI in the active space!

L active spin orbitals —> active orbitals

 $|\Psi^{\text{CASCI}}| = \sum c_{7} |\Phi_{7}|$





Virtual spin-orbitals "secondary"

CASCI is FCI in the active space!

active spin orbitals \rightarrow active orbitals

$$\Psi^{\text{CASCI}} = \sum \mathcal{C}_{\zeta} | \Phi_{\zeta} \rangle$$

Inactive spin orbitals "core"

How does it work for our H₂ example?







Multi-configurational wave function necessitate a re-optimisation of the orbitals!

Multi-Configurational Self-Consistent-Field (MCSCF) approach ΤU

Interatomic distance (a.u.)

CASCI / MCSCF for H₂

MCSCF: concepts and purpose

MCSCF - concepts I

- Introduce as small number of (active) orbitals: about 10-20 with occupation numbers n allowed to vary
- Active orbitals with occupations
- Select configurations (many-particle basis states) to include
- Form of the wave function (-> SD, ONVs or CSFs):

• OPTIMISE the orbitals <u>and</u> the CI coefficients, C_7

$$: \quad 0 \ll \eta \ll 2$$

$$|\Psi| = \sum C_{\zeta} |\Phi_{\zeta}|$$

MCSCF - concepts II

- Simplify general MCSCF ansatz by including all configurations generated by allocating all active electrons to these active orbitals: FCI in the active space $(\langle -\rangle CASCI!)$
- Picking a proper set of active orbitals is still required (can be automated too) but configuration generation is automated
- MCSCF optimisation based on this simplification is coined as *complete active space self-consistent field* — or simply CASSCF

MCSCF - purpose

- that arise as $r_{12} \rightarrow 0$, that is *dynamical correlation*
 - (i) configurational near-degeneracies and/or (ii) gross deficiencies in the RHF wave function

MCSCF does not describe the short-range correlation contributions

MCSCF aims at including non-dynamical correlation that arises from

Includes near-degenerate orbitals to account for static correlation

• Will in general not describe the complete correlation energy!

CASSCF: concepts, optimisation and limitations

CASSCF - concepts

- Definition of the orbital spaces follows from CASCI: inactive active and secondary
- The active orbital space should include:
 - all orbitals where the occupation number n changes significantly during a process (reaction, excitation, ionisation, ...)
 - orbitals where $0 \ll \eta \ll 2$
 - can be automated (overlap, orbital) entropy, perturbative estimates, ...) but do not underestimate "chemical intuition"

CASSCF - scaling

2	4
4	36
6	400
8	4.900
10	63.504
12	853.776
14	11.778.896
16	165.636.896
18	2.363.904.260
20	34.134.777.856
24	7.312.459.672.336

 The number of Slater determinant (or ONVs) $\{\phi\}$ scales for 2k electrons in 2k orbitals as

$$\{\boldsymbol{\Phi}\} = \begin{pmatrix} 2\boldsymbol{k} \\ \boldsymbol{k} \end{pmatrix}^2$$

• Largest calculation with standard CI: CAS(24,24), practical limit about (20, 20)!

 Larger CAS spaces require more advanced approaches (—> see The Present!)

CASSCF - active orbital spaces Simple diatomics

- Sometimes simple and intuitive like for H2: $(\sigma_q, \sigma_u)^2 \rightarrow CAS(2,2)$
- Ground state of N₂ (N=1s²2s²2p³) requires 2p orbitals: (σ_q , π_u , π_q , σ_u)⁶— > CAS(6,6)
- C₂/Be₂: require inclusion of 2s/2p shells because of near-degeneracies!
- Picking CAS for main-group dimers can be straightforward... but does not necessarily have to be the case
- Transition metal dimers are far from trivial! (-> see "The Present")

CASSCF - active orbital spaces Polyatomic molecules

- In general, including the full valence space is not an option (too many e/o)
- Simple guidelines:
 - Breaking a C-H or C-C bond in a hydrocarbon —> include ($\sigma \sigma^*$)²
 - Spectroscopy/reaction of aromatic/conjugated -systems —> include ($\pi \pi^*$)
- If even the minimal CAS reaches beyond (20,20), consider alternative approaches like DMRG, HCI, FCIQMC, selective CI, stocastic CI, ...

CASSCF - targeting individual states State-specific approach

- Goal: target individual excited states which are not the lowest states wrt spin and/or spatial symmetry
- Challenges:
 - Requires convergence of optimisation algorithm to a saddle point
 - Root flipping: excited state may become the lowest state in CI along a path
 - Converged MCSCF/CASSCF wave functions for two roots of the same symmetry (spatial/spin) are in general NOT orthogonal! —> use *state-interaction* to calculate properties: SOC, NAC, ...

CASSCF - targeting an ensemble of states State-average approach

- Goal: target an ensemble of star spatial symmetry
 - Introduce a weighted ensemble {M}_{\u03c0} of the energies of M states: $E^{SA} = \sum_{i=1}^{M} \omega_i E_i$
 - Each state in $\{M\}_{\omega}$ will have identical MOs but different CI coefficients not variational
- Challenge: MOs in different states may be very different
 —> may require larger CAS to ensure smooth convergence

Goal: target an ensemble of states simultaneously wrt spin and/or

CASSCF - targeting an ensemble of states State-average approach

- state):
 - CAS: $(\pi_u \pi_g)^2$
 - Character of N state: $|\psi\rangle$
 - Character of V state:
- N and V state —> different spatial extents (= 1.7 / 9.1)
- Cannot be described by a single set of π orbitals!

• Example: consider an SA-CAS(2,2)SCF calculation of ethylene (C₂H₄) for the singlet (S=0) ground ("N state") and lowest excited state ("V

CASSCF - Optimisation of the wave tonettion

• Wave function ansatz (note change of notation :

(normalisation!):

 $0 = \sum C_{\mathcal{L}} \vee \Phi_{\mathcal{L}}$ Determine the MO and CI coefficients using the variational principle

CASSCF - Optimisation of the wave function Energy

$$D_{pq} = \left\langle 0 \left| \hat{E}_{pq} \right| 0 \right\rangle \text{(first-order RDM)}$$
$$P_{pqrs} = \frac{1}{2} \left\langle \tilde{0} \left| \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \right| \tilde{0} \right\rangle$$

• MO coefficients $\{\tilde{\varphi}\}$ appear in h_{pq} and g_{pqrs} , CI coefficients $\{\tilde{\Phi}\}$ in **D** and **P**

 $= \sum h_{pq} D_{pq} + \sum g_{pqrs} P_{pqrs} + h_{nuc}$ pqrs

A)

(second-order RDM)

CASSCF - Optimisation of the wave function Unitary transformations of MOs

 MOs are orthonormal —> unitary transformation ensures orthonormality

- Write as with , that is is anti-hermitian $\hat{T} = \sum_{pq} T_{pq} E_{pq} = \sum_{p>q} T_{pq} (E_{pq} - E_{qp})$
- Transformation of creation operators: $\mathcal{A}_{\underline{x}} = \exp(\mathcal{T}) \mathcal{A}_{p}^{\dagger} \exp(-\mathcal{T})$
- CAS —> we only need the following rotation parameters: $\{\}, \{\}, \{\}\}$

 $\mathscr{O} = \mathscr{O} U$ with $U^{\dagger} U = \mathbf{1}$

CASSCF - Optimisation of the wave formations of CI vectors

• Cl vector(s) are normalised:

$$0 = \sum_{\zeta} C_{\zeta} \vee \Phi_{\zeta}$$

- Complementary space orthogonal to :
- Define anti-hermitian operator :

with $\sum_{\zeta} \vee C_{\zeta} \square^2 = 1$

• Unitary transformation of such that remains normalised

 $\tilde{\mathbf{O}} = \exp(\mathbf{S}) \vee \mathbf{O} \mathbf{J}$

CASSCF - Optimisation of the wave function Concepts

- Resulting wave function ansatz: $\tilde{0} = \exp(7)$
- "Double"-exponential parametrisation with parameters
- Energy function with parameter space

$$E(\mathbf{p}) = E(\mathbf{T}, \mathbf{S}) = \mathbf{i} \circ \mathbf{v} + \mathbf{v} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{v} + \mathbf{v} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{v} \exp(-\mathbf{S}) \exp(-\mathbf{T}) + \mathbf{i} \exp(\mathbf{T}) \exp(\mathbf{S}) + \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{v} + \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i} \circ \mathbf{i} = \mathbf{i} \circ \mathbf{i$$

$$(\mathbf{S}) \exp(\mathbf{S}) \vee \mathbf{0}$$

CASSCF - Optimisation of the wave **futmatienergy**

- Vary parameters and such that energy becomes stationary:
- Leads to a set of nonlinear equation
- In the following, we examine the Newton-Raphson method for CASSCF optimisation

$$= 0 \frac{\partial E}{\partial S_{K^0}} = 0$$

Itions that must be solved iteratively

CASSCF - Optimisation of the wave function Optimal energy

becomes stationary:

- Leads to a set of nonlinear equations that must be solved iteratively
- In the following, we examine the Newton-Raphson method for CASSCF optimisation

• Vary parameters T and S such that energy $E(T, S) = \langle 0 | e^{-\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} e^{\hat{S}} | 0 \rangle$

 $\frac{\partial E}{\partial T_{pq}} = 0 \quad \frac{\partial E}{\partial S_{K0}} = 0$

CASSCF - Optimisation of the wave femotion by method - concepts II

Approximation to stationary point by finding stationary point of :

$$\frac{\partial E^{(2)}}{\partial p_i} = 0 \rightarrow g + E$$

- For the current , compute new gradient and Hessian
- Continue iterative procedure until
- Note:
 - Approximating with is only valid for small
 - Quadratic convergence for small

$Hp=0 \rightarrow p=-H^{-1}g$

alid for small

CASSCF - Optimisation of the wave function Newton-Raphson method - concepts II

- Approximation to stationary point by finding stationary point of $E^{(2)}$: $\frac{\partial \mathcal{L}^{(-)}}{\partial p_i} = 0 \rightarrow \mathbf{g} + \mathbf{H}\mathbf{p} = \mathbf{0} \rightarrow \mathbf{p} = -\mathbf{H}^{-1}\mathbf{g}$
- For the current **p**, compute new gradient and Hessian
- Continue iterative procedure until $|\mathbf{g}| \approx 0$

• Note:

- Approximating E with $E^{(2)}$ is only valid for small \mathbf{p}
- Quadratic convergence for small **p**

CASSCF - Optimisation of the wave function Taylor expansion of the energy

• **Recall:** BCH expansion for operators $\exp(-\hat{A})\hat{B}\exp(\hat{A}) = \hat{B} + \hat{B}$

• Expand E through second order in \hat{T}, \hat{S} with E(0), g and H parts

 $E^{(2)}(\mathbf{T},\mathbf{S}) = \left\langle 0 \left| \hat{H} \right| 0 \right\rangle + \left\langle 0 \left| \left[\hat{H}, \hat{T} \right] + \left[\hat{H}, \hat{S} \right] \right| 0 \right\rangle$

$$\left[\hat{B},\hat{A}\right] + \frac{1}{2} \left[\left[\hat{B},\hat{A}\right],\hat{A} \right] + \dots$$

$+\left\langle 0 \left| \frac{1}{2} \left[\left[\hat{H}, \hat{T} \right], \hat{T} \right] + \frac{1}{2} \left[\left[\hat{H}, \hat{S} \right], \hat{S} \right] + \left[\left[\hat{H}, \hat{T} \right], \hat{S} \right] \right| 0 \right\rangle$

CASSCF - Optimisation of the wave **Eble at any and capabilities**

- DALTON: NR and other optimization techniques -> state-specific MCSCF
- OpenMolcas: no couplings —> state-specific + state-average MCSCF
- MOLPRO: second-order optimisation -> state-specific + state-average MCSCF
- ORCA: second-order optimisation -> state-specific + state-average MCSCF
- pySCF: quasi-second order \rightarrow state-specific + state-average MCSCF

Dynamical electron correlation combined with static correlation

Dynamical correlation combined with

- GOAL: treat dynamical correlation in combination with MCSCF wave function
 - simultaneously (diagonalize-and-perturb)
 - a posteriori (diagonalize-then-perturb)
- Should preferably be both size-extensive and size-consistent
 - size-extensive: energy scales linearly with number of particles N
 - size-consistent:

Dynamical correlation combined with MCSCF A not-so-complete summary ...

- Multi-reference CI:
 - Based on excitations out of a MC state
 - Variational but not size-consistent/size-extensive
- Multi-reference perturbation (MRPT2) theories: CASPT2, NEVPT2, ...
 - Based on (internally contracted) excitations out of a (or several) MC state
 - Differ in form of \hat{H}_0 and form of wave function corrections
 - (Nearly) size-extensive
- MRCC: less developed but most rigorous!
- post-MCSCF on-top pair-DFT correction (MC-pDFT)
 - Requires specialised DFAs
 - Works for SS and SA MC reference wave functions
- srDFT-IrMCSCF:
 - Requires specialised DFAs
 - Allows a simultaneous treatment of static and dynamic correlation