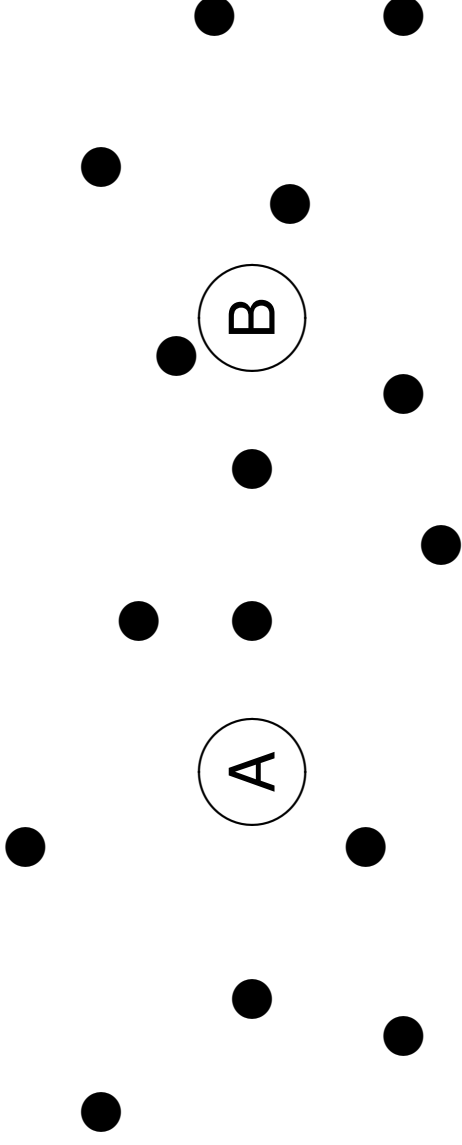


# **An Introduction to *ab initio* Theories**

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# The electronic problem



How can the properties of such a system be determined?

## Terminology

- Operators

$$\mathcal{O}a(x) = b(x)$$

- Dirac's short-hand notation

$$a(x) \equiv |a\rangle \quad a^* \equiv \langle a|$$

$$\Psi_i(x) \equiv |i\rangle \quad \Psi_i^* \equiv \langle i|$$

$$\int dx a^*(x)b(x) \equiv \langle a|b\rangle$$

## Terminology

- Orthonormality

$$\langle i|j\rangle = \delta_{ij} \quad \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases} \quad (\text{Kronecker Delta})$$

- Eigenvalues and eigenfunctions

$$\mathcal{O}|a\rangle = \omega_a|a\rangle$$

$$\mathcal{H}|\Psi\rangle = \mathcal{E}|\Psi\rangle$$

## Terminology

- Variational principle

$$\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1 \quad (\text{normalized trial function})$$

$$\langle \tilde{\Psi} | \mathcal{H} | \tilde{\Psi} \rangle = E_0 \geq \mathcal{E}_0 = \langle \Psi | \mathcal{H} | \Psi \rangle$$

# The Schrödinger equation

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

$$\begin{aligned} \mathcal{H} = & - \underbrace{\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_{elec}} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_i^2}_{T_{nuc}} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{elec-nuc}} \\ & + \underbrace{\sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}}}_{V_{elec-elec}} + \underbrace{\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{V_{nuc-nuc}} \end{aligned}$$

# The Born-Oppenheimer approximation

$$T_{nuc} \approx 0$$

$$V_{elec-nuc} \approx const$$

$$\mathcal{H}_{elec} = - \underbrace{\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_{elec}} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{elec-nuc}} + \underbrace{\sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}}}_{V_{elec-elec}}$$

## Electron spin and the Pauli principle

$$\chi(\mathbf{x}) = \chi(\mathbf{r}, \omega) \quad (\text{spin orbital})$$

$$= \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$



## Antisymmetry principle

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

$$\Psi(\mathbf{x}) = (N!)^{-\frac{1}{2}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \dots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \dots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \dots & \chi_k(x_N) \end{vmatrix}$$

Slater determinant

## Hartree-Fock theory

- Has played an important role in modern chemistry
- Usually first step in more accurate calculations
- Wavefunction is approximated by a single Slater determinant  $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle$
- Energy  $E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$  is minimized with respect to spin orbitals (variational principle)

# The Hartree-Fock equations

$$f(i)\chi(\mathbf{x}_i) = \varepsilon\chi(\mathbf{x}_i)$$

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i)$$

$f(i) \rightarrow$  one electron operator

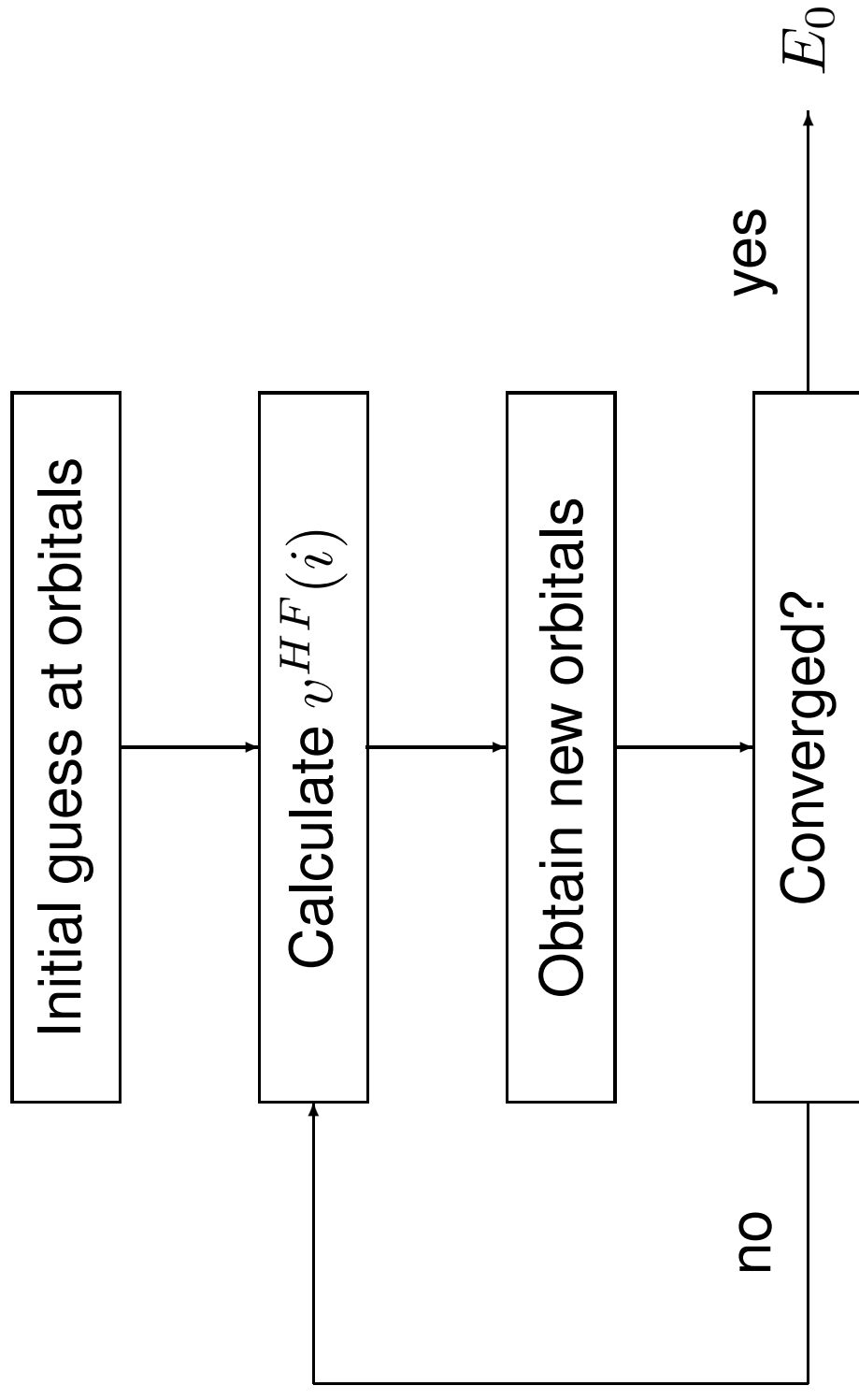
$v^{HF}(i) \rightarrow$  average potential due to other electrons

## Hartree-Fock potential

$$v^{HF}(i) = v^{HF}(i) [\chi(\mathbf{x}_1), \dots, \chi(\mathbf{x}_{i-1}), \chi(\mathbf{x}_{i+1}), \dots, \chi(\mathbf{x}_N)]$$

- Many-electron problem reduced to N one-electron problems
- Electron-electron repulsion treated in an average way
- Iterative solution due to non-linearity (SCF)

## The “Self Consistent Field” procedure



## Introduction of a basis set

- Set of spatial basisfunctions  $\{\phi_\mu(\mathbf{r}) \mid \mu = 1, 2, \dots, K\}$
- Expansion of  $\psi_i$  as  $\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu$
- Matrix eigenvalue equations for  $C_{\mu i}$
- HF ground state  $|\Psi_0\rangle = |\chi_1, \chi_2, \dots, \chi_N\rangle$
- HF limit obtained for  $K \rightarrow \infty$

## Accuracy of the HF approximation

- Nowadays usually not accurate enough
- Sometimes qualitatively wrong (i.e. dipole moment of CO)
- Mainly used as starting point for post-HF methods

## Improving upon Hartree-Fock theory

- Better description of electron-electron interaction (correlation) by post HF methods

$$\begin{aligned} E_{corr} &= \mathcal{E}_0 - E_0 \\ &= \mathcal{E}_0 - \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle \end{aligned}$$



## Configuration interaction

- $|\Psi_0\rangle$  is just one of many possible determinants
- There are  $\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$  different determinants
- $|\Psi_i\rangle$  can be described by difference to  $|\Psi_0\rangle$

$$\begin{aligned}
 |\Psi_0\rangle &= |\chi_1, \chi_2, \dots, \chi_a, \chi_b, \dots, \chi_N\rangle && \text{HF reference} \\
 |\Psi_a^r\rangle &= |\chi_1, \chi_2, \dots, \chi_r, \chi_b, \dots, \chi_N\rangle && \text{singly excited} \\
 |\Psi_{ab}^{rs}\rangle &= |\chi_1, \chi_2, \dots, \chi_r, \chi_s, \dots, \chi_N\rangle && \text{doubly excited} \\
 &\vdots &&
 \end{aligned}$$

## The CI wavefunction

- $\{|\Psi_i\rangle\} = \{|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, \dots\}$  is a complete set for the expansion of any N-electron wavefunction
- Thus the exact wavefunction  $|\Phi\rangle$  can be written as

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_a^r c_a^r |\Psi_a^r\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots$$

## Results from FCI calculations

- *exact* energy of the ground state and all excited states
- $\mathcal{E}_0$  can be calculated to benchmark other methods

However:

- Devastating scaling behaviour
- Limited to very small systems and basis sets

## Truncated single-reference CI

- Computationally more feasible than FCI
- HF ground state  $|\Psi_0\rangle$  taken as reference
- Most important contributions from double excitation (CID)
- Size consistency problems

## Multi-reference CI (MCSCF)

$$|\Psi_{MCSCF}\rangle = \sum_I c_I |\Psi_I\rangle$$

- Normally only a small number of configurations is included (called “active space” in CASSCF)
- $c_I$  and orbitals in  $|\Psi_I\rangle$  are optimized
- If only one determinant included, identical to HF
- $|\Psi_{MCSCF}\rangle$  can be a starting point for MR correlation

## Improving upon truncated CI

“How to truncate FCI elegantly and efficiently?”

- Method must be size consistent
- Possibly recover higher order terms obtainable from lower order terms (i.e. quadruples from doubles)

# Coupled cluster theory

$$|\Phi_{CC}\rangle = e^{\mathcal{T}} |\Psi_0\rangle$$

with  $\mathcal{T} = \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{T}_3 + \dots$  (cluster operator)

$$\mathcal{T}_1 = \sum_a^r c_a^r a_r^\dagger a_a$$

$$\mathcal{T}_2 = \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab \\ rs}} c_{ab}^{rs} a_s^\dagger a_r^\dagger a_b a_a$$

...

## Restriction to double excitations (CCD)

$$|\Phi_{CCD}\rangle = e^{\mathcal{T}_2} |\Psi_0\rangle$$
$$\mathcal{T}_2 = \frac{1}{4} \sum_{ab} \sum_{rs} c_{ab}^{rs} a_s^\dagger a_r^\dagger a_b a_a$$

Maclaurin expansion of  $e^{\mathcal{T}}$ :

$$e^x = 1 + x + \frac{1}{2}x^2 + \dots = \sum_{n=0}^{\infty} \frac{1}{n!} x^n$$



## Maclaurin expansion of $|\Psi_{CCD}\rangle$

$$\begin{aligned}
 |\Phi_{CCD}\rangle = & \left[ 1 + \frac{1}{4} \sum_{\substack{ab \\ rs}} c_{ab}^{rs} a_s^\dagger a_r^\dagger a_b a_a \right. \\
 & + \frac{1}{32} \sum_{\substack{abcd \\ rstu}} c_{abcd}^{rstu} a_s^\dagger a_r^\dagger a_b a_a a_u^\dagger a_t^\dagger a_d a_c \\
 & + \frac{1}{384} \sum_{\substack{abcdef \\ rstuvw}} c_{abcdef}^{rstuvw} a_s^\dagger a_r^\dagger a_b a_a a_u^\dagger a_t^\dagger a_d a_c a_w^\dagger a_v^\dagger a_f a_e \\
 & \left. + \dots \right] |\Psi_0\rangle
 \end{aligned}$$

## Maclaurin expansion of $|\Psi_{CCD}\rangle$

$$|\Phi_{CCD}\rangle = |\Psi_0\rangle + \sum_{\substack{a < b \\ r < s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a < b < c < d \\ r < s < t < u}} c_{ab}^{rs} * c_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots$$

$c_{ab}^{rs} * c_{cd}^{tu}$  → sum of all possible products of doubly excited coefficients

## Final CCD equations

Projection onto  $|\Psi_0\rangle$  and all excited determinants ( $|\Psi_{ab}^{rs}\rangle$ )

- Multiplying by  $\langle\Psi_0|$

$$\begin{aligned}\langle\Psi_0|\mathcal{H} - E_0|\Phi_{CCD}\rangle &= E_{corr} \langle\Psi_0|\Phi_{CCD}\rangle \\ \sum_{\substack{c<d \\ t<u}} \langle\Psi_0|\mathcal{H}|\Psi_{cd}^{tu}\rangle c_{cd}^{tu} &= E_{corr}\end{aligned}$$

## Final CCD equations

- Multiplying by  $\langle \Psi_{ab}^{rs} |$

$$\langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Phi_{CCD} \rangle = E_{corr} \langle \Psi_{ab}^{rs} | \Phi_{CCD} \rangle$$

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \mathcal{H} | \Psi_0 \rangle + \sum_{\substack{c < d \\ t < u}} \langle \Psi_{ab}^{rs} | \mathcal{H} - E_0 | \Psi_{cd}^{tu} \rangle \\ - \sum_{\substack{c < d \\ t < u}} \langle \Psi_0 | \mathcal{H} | \Psi_{ab}^{tu} \rangle \langle C_{ab}^{rs} * C_{cd}^{tu} \rangle = 0 \end{aligned}$$

## Comparison of CC and CI

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	CID	CCD
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size consistent	no	yes
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higher excitations	no	through $\mathcal{J}_2^2$
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- In CC quadruple excitations are generated by
$$\mathcal{J}_4 + \mathcal{J}_3\mathcal{J}_1 + \frac{1}{2}\mathcal{J}_2^2 + \frac{1}{2}\mathcal{J}_2\mathcal{J}_1^2 + \frac{1}{24}\mathcal{J}_1^4$$
- Superior description by coupled cluster theory

## Deviation from FCI results

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[mH]	SCF	CID	CISD	CISDT	CISDTQ	CCD	CCSD	CCSDT	CCSDTQ
BH	102.4	6.02	5.21	3.60	0.03	2.72	1.79	0.07	0.00
HF	203.9	10.3	9.38	7.01	0.28	3.76	3.01	0.27	0.02
H <sub>2</sub> O	216.1	13.7	12.9	10.6	0.40	5.01	4.12	0.53	0.02

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⇒ CISDTQ needed to outperform CCD

## Reduction of computational cost

$$\text{CCSD} \sim N^6$$

$$\text{CCSDT} \sim N^8$$

$$\text{CCSDTQ} \sim N^{10}$$

- Basis must be CCSD
- But: triple contribution not negligible
- Thus: eliminate all steps  $> N^6$  from iteration

## The CCSD(T) model

$$E = E_{CCSD} + \Delta E_T$$

- $\Delta E_T$  taken from MBPT4 using CCSD-coefficients
- Additional 5th-order term to damp triple exaggeration
- Only one  $N^7$ -step
- Gives excellent performance



## Further remarks

- Limited to small to medium sized molecules
- Huge amounts of memory and disk required
- Not very well suited for open-shell molecules
- $T_1$ -diagnostic helpful in determining multi-reference character ( $T_1 > 0.02$ ).

## **Choice of a basis set**

- Large basis sets with many polarization functions required for post-HF calculations
- For CBS extrapolation systematic behaviour required
- Pople's basis sets discouraged
- Dunning's correlation consistent basis sets recommended

## Correlation consistent basis sets

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	contractions	augmentation
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vdz	[3s2p1d]	[spd]
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vtz	[4s3p2d1f]	[spdf]
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vqz	[5s4p3d2f1g]	[spdfg]
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v5z	[6s5p4d3f2g1h]	[spdfgh]
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- Systematic recovery of  $E_{corr}$
- Available up to 7-tuple level with different sets of augmenting functions

## Wn-theory

- Very accurate calculation of TAEs and heats of formation
- Extrapolation of CCSD(T) energy to CBS limit
- Incorporates core correlation and scalar relativistic effects
- Designed to reach chemical accuracy ( $\approx 1$  kJ/mol)

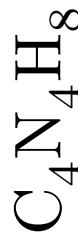
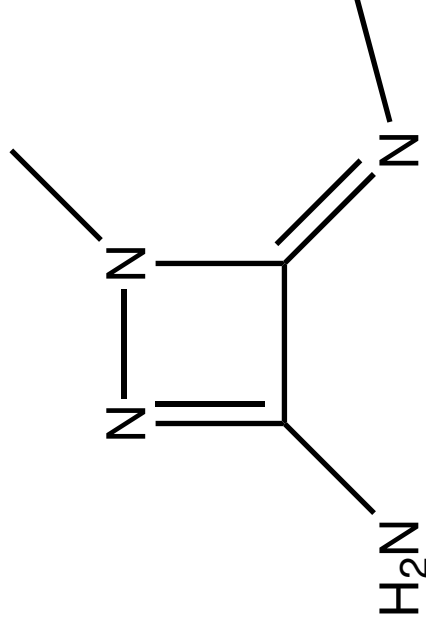
## Protocol for Wn-theory

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	W2	W1
geometry	ccsd(t)/vqz+1	b3lyp/vtz+1
ZPE	ccsd(t)/vtz+1 anharmonic	b3lyp/vtz+1 scaled
Energy	ccsd(t)/avtz+2d1f	ccsd(t)/avdz+2d
	ccsd(t)/avqz+2d1f	ccsd(t)/avtz+2d1f
	ccsd/av5z+2d1f	ccsd/avqz+2d1f
core correlation	ccsd(t)/MTsmall	
relativistic effects	acpf/MTsmall	
MAE	0.23 kcal/mol	0.30 kcal/mol

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## Illustrative W1h calculation



44 valence and 16 core electrons

## Illustrative W1h calculation

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	vdz	vtz	vqz
AOs	272	592	1 100
contractions	152	416	780
	<i>two-electron integrals</i>		
time [h]	0:00 / 0:02	0:18 / 9:36	0:00 / 0:00
disk [MB]	1 130	54 190	27
	<i>Hartree-Fock SCF</i>		
time [h]	0:02 / 0:02	1:41 / 43:09	11:50 / 11:51
disk [MB]	1 130	54 190	120
$E_{hf}$	-373.77995582	-373.88566959	-373.90859562

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	vdz	vtz	vqz
<i>CCSD / CCSD(T)</i>			
CSFs	3 605 955	36 069 771	136 149 751
time [h]	1:40 / 1:41	93:58 / 179:36	391:34 / 450:00
triples [h]	0:56	63:48	
disk [MB]	1 190	54 190	33 820
$E_{ccsd}$	-375.04646268	-375.41640145	-375.90859562
$E_{ccsd(t)}$	-375.10183150	-375.50014101	
$T_1$	0.0157	0.0160	0.0160

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## References

- [1] A. Szabo, N. S. Ostlund, *Modern Quantum Chemistry*, Dover Publications, Inc., Mineola, New York, **1996**.
- [2] P. von Ragué Schleyer (Ed.) *Encyclopedia of Computational Chemistry*, John Wiley & Sons, Chichester, **1998**.
- [3] J. M. L. Martin, G. de Oliveira, *J. Chem. Phys.* **1999**, *111*, 1843–1856.