Chimica Computazionale

Introduction to computational chemistry

Emanuele Coccia

UNIVERSITÀ DEGLI STUDI DI TRIESTE

DSCF Dipartimento di Scienze Chimiche e Farmaceutiche

PhotoInduced Quantum Dynamics (PIQD) Group

Definition of computational chemistry

Computational chemistry

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  - Transformation of matter
  - Properties of atoms, molecules and materials

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- Theoretical chemistry:
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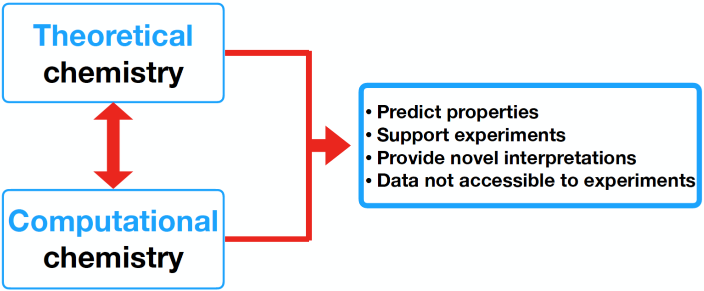
  - Processes of chemical relevance
- Numerical approaches needed to find approximate solutions to theory
- Computational chemistry: computer as a research tool



Theory, models and computation

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  - Rules to describe the behavior of physical systems
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- Models:
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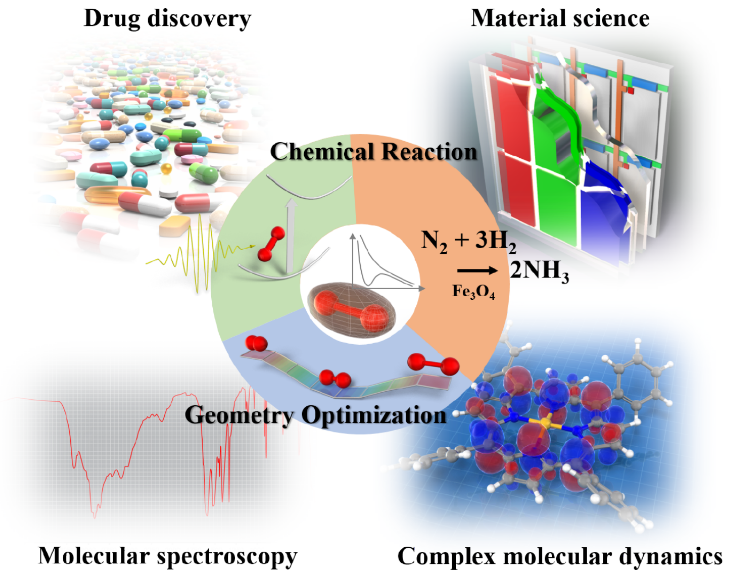
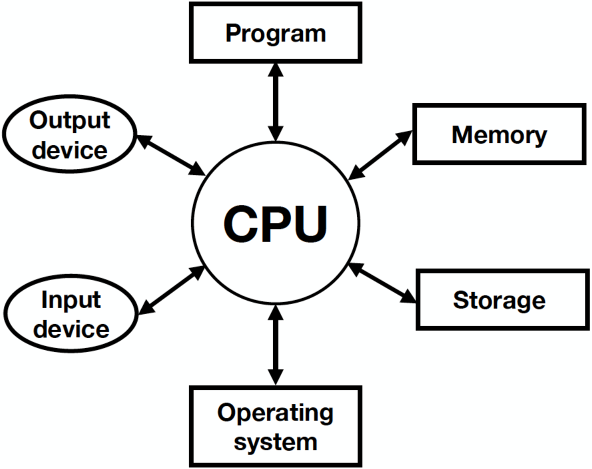
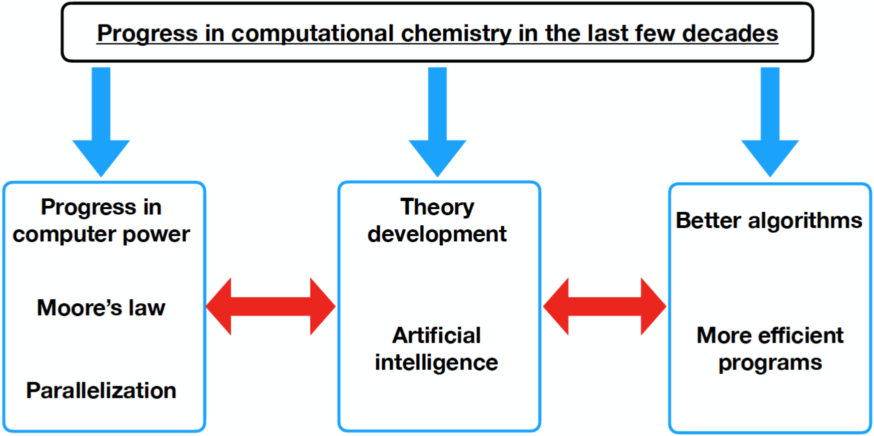
- Computation:
  - Use of digital technology to solve equations for a theory or model
  - Focus (also) on efficiency in simulations
  - Apply theory/models to increasingly complex systems

Computational chemistry





- Programs of computational chemistry written with: Fortran, C, C++, Python etc.


Progress in computational chemistry in the last few decades
Progress in computer power
Moore's law
Parallelization
Theory development
Artificial intelligence
Better algorithms
More efficient programs

Designing a computational project

1. Defining an aim

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4. Being critical of the computational results
5. Testing the calculations

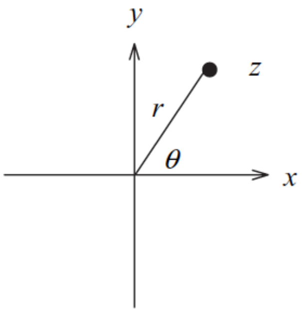
Atomic units

Symbol	Quantity	Value in au	Value in SI units
m_e	Electron mass	1	9.110×10^{-31} kg
e	Electron charge	1	1.602×10^{-19} C
t	Time	1	2.419×10^{-17} s
$\hbar$	$h/2\pi$ (atomic momentum unit)	1	1.055×10^{-34} J s
h	Planck's constant	2π	6.626×10^{-34} J s
a_0	Bohr radius (atomic distance unit)	1	5.292×10^{-11} m
E_H	Hartree (atomic energy unit)	1	4.360×10^{-18} J
c	Speed of light	137.036	2.998×10^{8} m/s
α	Fine structure constant ($= e^2/\hbar c 4\pi\varepsilon_0 = 1/c$)	0.00729735	0.00729735
μ_B	Bohr magneton ($= e\hbar/2m_e$)	$^1/_2$	9.274×10^{-24} J/T
μ_N	Nuclear magneton	2.723×10^{-4}	5.051×10^{-27} J/T
$4\pi\varepsilon_0$	Vacuum permittivity	1	1.113×10^{-10} C^2/J m
μ_0	Vacuum permeability ($4\pi/c^2$)	6.692×10^{-4}	1.257×10^{-6} N s^2/C^2

Math overview

Math overview

- Complex number $z = x + iy$, x and y are real numbers, $i^2 = -1$



$$z = x + iy$$
$$z = re^{i\theta} = r\cos(\theta) + ir\sin(\theta)$$

- Complex conjugate $z^* = x - iy$ or $z^* = re^{-i\theta}$

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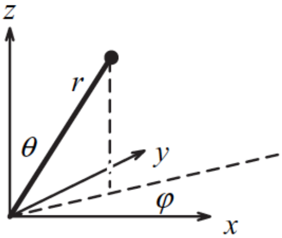

$$x = r \sin\theta \cos\varphi$$
$$y = r \sin\theta \sin\varphi$$
$$z = r \cos\theta$$

- Cartesian and polar systems

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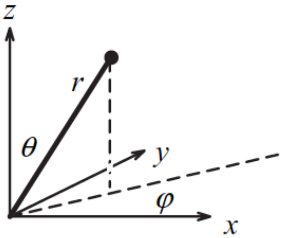

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- Cartesian and polar systems
- velocity $\mathbf{v} = \{v_x, v_y, v_z\} = \{\frac{\partial x}{\partial t}, \frac{\partial y}{\partial t}, \frac{\partial z}{\partial t}\}$

- matrix: two-dimensional set of numbers (Hessian etc.)

$$\begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

- adjoint matrix: complex conjugate of the transpose
- Hermitian matrices in quantum chemistry are self-adjoint, e.g. $\mathbf{H} = \mathbf{H}^\dagger$
- with real elements, the matrix is symmetric, $\mathbf{H} = \mathbf{H}^T$

Math overview

- Row-by-column matrix-matrix multiplication **AB**

$$\mathbf{AB} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{11}b_{11} + a_{21}b_{22} \end{pmatrix}$$

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- Determinant $|\mathbf{A}|$ for a 2×2 matrix (only square matrices!)

$$|\mathbf{A}| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$$

$$\begin{aligned} |\mathbf{A}| &= \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \\ &= a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} \\ &= a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} \\ &+ a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{13}a_{22}a_{31} \end{aligned}$$

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- System of linear equations $\mathbf{A}\mathbf{x} = \mathbf{b}$

$$\begin{aligned}
a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= b_1 \\
a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= b_2 \\
\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots &= \vdots \\
a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n &= b_n
\end{aligned}$$

- $\mathbf{x} = \mathbf{A}^{-1}\mathbf{b}$

Math overview

- Function $E(\mathbf{R})$: $\mathbf{R} \rightarrow E$
- Functional $E_{xc}[\rho(\mathbf{x})]$: $\mathbf{x} \rightarrow \rho \rightarrow E_{xc}$
- Operator $\hat{O}$: a function from another function
- Hilbert space: functions or operators as vectors
- Bra-ket notation

$$\begin{aligned} \text{bra} : \langle \mathbf{f} | \mathbf{x} \rangle &= \mathbf{f}^*(\mathbf{x}) \\ \text{ket} : \langle \mathbf{x} | \mathbf{f} \rangle &= \mathbf{f}(\mathbf{x}) \end{aligned}$$

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\langle \mathbf{f} | \mathbf{g} \rangle &= \int \mathbf{f}^*(\mathbf{x}) \mathbf{g}(\mathbf{x}) d\mathbf{x} \\
|\mathbf{f}(\mathbf{x})| = \sqrt{\langle \mathbf{f} | \mathbf{f} \rangle} &= \sqrt{\int \mathbf{f}^*(\mathbf{x}) \mathbf{f}(\mathbf{x}) d\mathbf{x}}
\end{aligned}
$$

Math overview

- Functions and operators with bra-ket notation

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Linear operators

$$\begin{aligned} \hat{O}(\mathbf{f}+\mathbf{g}) &= \hat{O}\mathbf{f}+\hat{O}\mathbf{g} \\ \hat{O}(c\mathbf{f}) &= c\hat{O}\mathbf{f} \end{aligned}$$

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- Normalization

$$\begin{aligned} \langle \mathbf{f}|\mathbf{f}\rangle &= N^2 \\ \mathbf{f}' &= N^{-1}\mathbf{f} \\ \langle \mathbf{f}'|\mathbf{f}'\rangle &= 1 \end{aligned}$$

- Orthogonalization (orthonormalization)

$$\langle \mathbf{f}_i|\mathbf{f}_j\rangle = \delta_{ij}$$