

**Density Functional Theory:
Models and numerical methods**

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Ecole des Ponts and INRIA, Paris, France

Beijing, June 7-10, 2017

First-principle molecular simulation is used by thousands of physicists, chemists, biologists, materials scientists, nanoscientists on a daily basis:

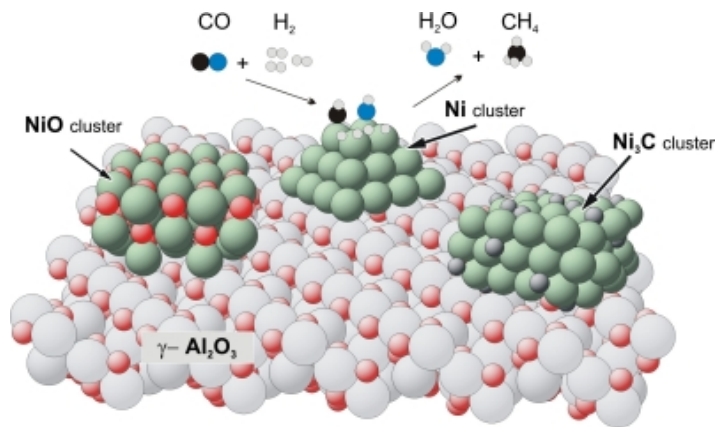
- **over 20,000 papers a year and growing;**
- **about 20% of the resources available in scientific computing centers;**
- **Kohn and Pople were awarded the 1998 Nobel prize in Chemistry for their contributions to electronic structure calculation methods (Density Functional Theory and wavefunction methods).**
- **Karplus, Levitt and Warshel were awarded the 2013 Nobel prize in Chemistry for their contributions to multiscale modeling of (bio)molecules.**

Most of these models are completely, or largely, unexplored from mathematical and numerical points of view.

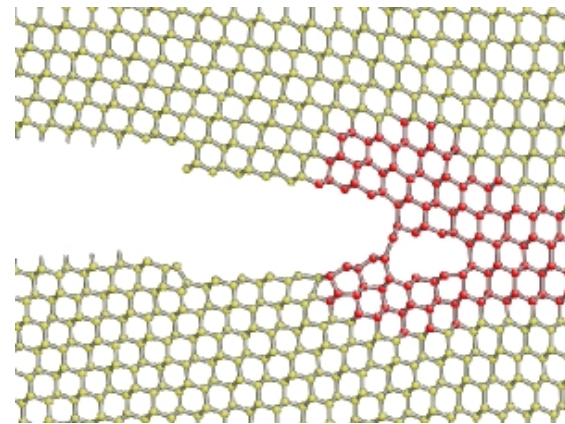
Number of hits (June 2017)

	Web of Science	MathSciNet	% in MathSciNet
"Density Functional Theory"	136,840	342	0.2 %
"fluid dynamics"	50,989	10,752	21 %
"Navier-Stokes"	48,412	20,442	42 %
"Boltzmann equation"	12,842	4,829	37 %
"Maxwell equations"	6,714	4,004	59 %

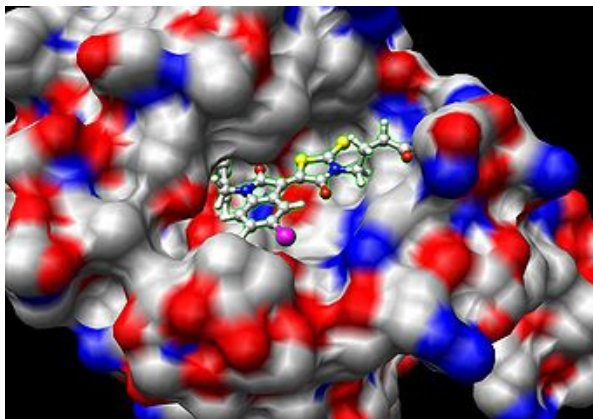
Examples of application



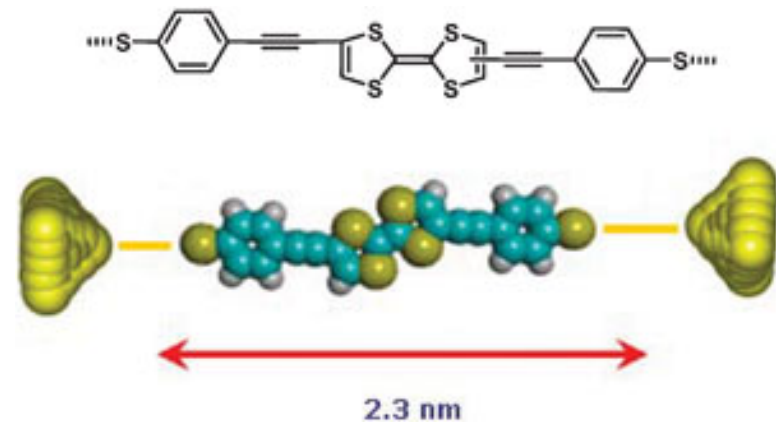
Chemistry



Materials science



Molecular biology



Nanotechnology

Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																								
1 H Hydrogen 1.00794	Atomic # Name Symbol Atomic Mass																2 He Helium 4.002602																								
3 Li Lithium 6.941	4 Be Beryllium 9.012182	<div style="display: flex; justify-content: space-between;"> <div style="width: 20%;"> <p>C Solid</p> <p>Hg Liquid</p> <p>H Gas</p> <p>Rf Unknown</p> </div> <div style="width: 60%; border: 1px solid black; padding: 5px;"> <p style="text-align: center;">Metals</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="background-color: #FFD700; text-align: center;">Alkali metals</td> <td style="background-color: #FFD700; text-align: center;">Alkaline earth metals</td> <td style="background-color: #FFDAB9; text-align: center;">Lanthanoids</td> <td style="background-color: #FFDAB9; text-align: center;">Transition metals</td> <td style="background-color: #ADD8E6; text-align: center;">Poor metals</td> </tr> <tr> <td colspan="2"></td> <td style="background-color: #FFDAB9; text-align: center;">Actinoids</td> <td></td> <td></td> </tr> </table> </div> <div style="width: 20%;"> <p style="background-color: #90EE90; text-align: center;">Other nonmetals</p> <p style="background-color: #ADD8E6; text-align: center;">Noble gases</p> </div> </div>																Alkali metals	Alkaline earth metals	Lanthanoids	Transition metals	Poor metals			Actinoids			5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050	13 Al Aluminium 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
Alkali metals	Alkaline earth metals	Lanthanoids	Transition metals	Poor metals																																					
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19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798																								
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293																								
55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0178)																								
87 Fr Francium (223)	88 Ra Radium (226)	89-103	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (288)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)																								

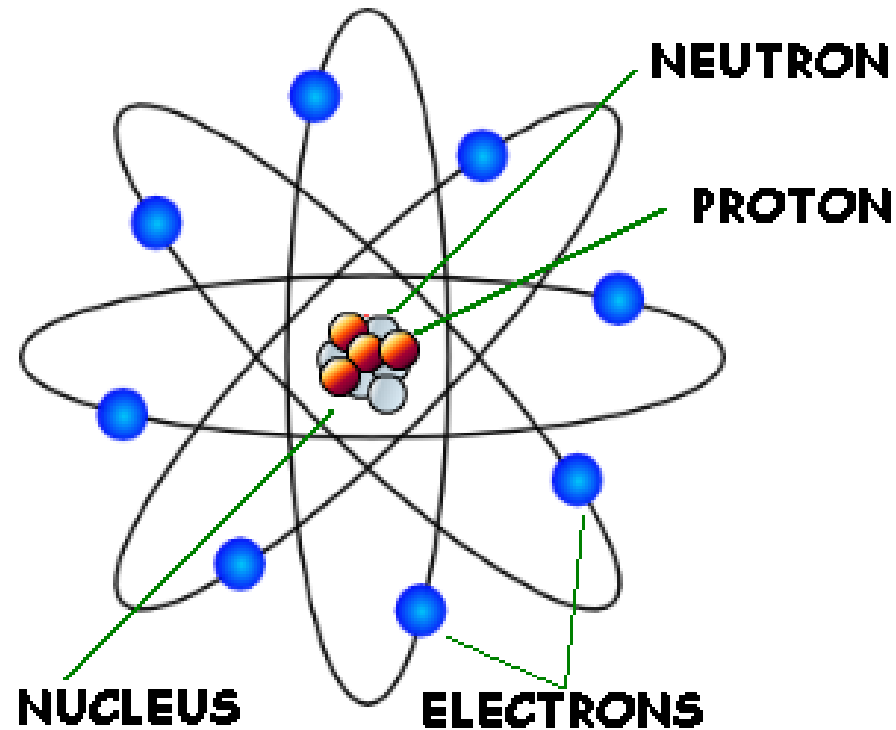
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Internal structure of an atom



In the absence of nuclear reactions,

nuclei can be considered as "elementary particles".

Key observation: a molecular system is nothing but a collection of M atomic nuclei and N electrons in Coulomb interaction.

Such a system can be described by the laws of quantum mechanics (many-body Schrödinger equation) and statistical physics.

Example of the water molecule (H₂O): $M = 3$ atomic nuclei (1 oxygen + 2 hydrogens) and $N = 10$ electrons.

The only parameters of these models are (atomic units)

- a few fundamental constants of physics

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad \varepsilon_0 = (4\pi)^{-1},$$

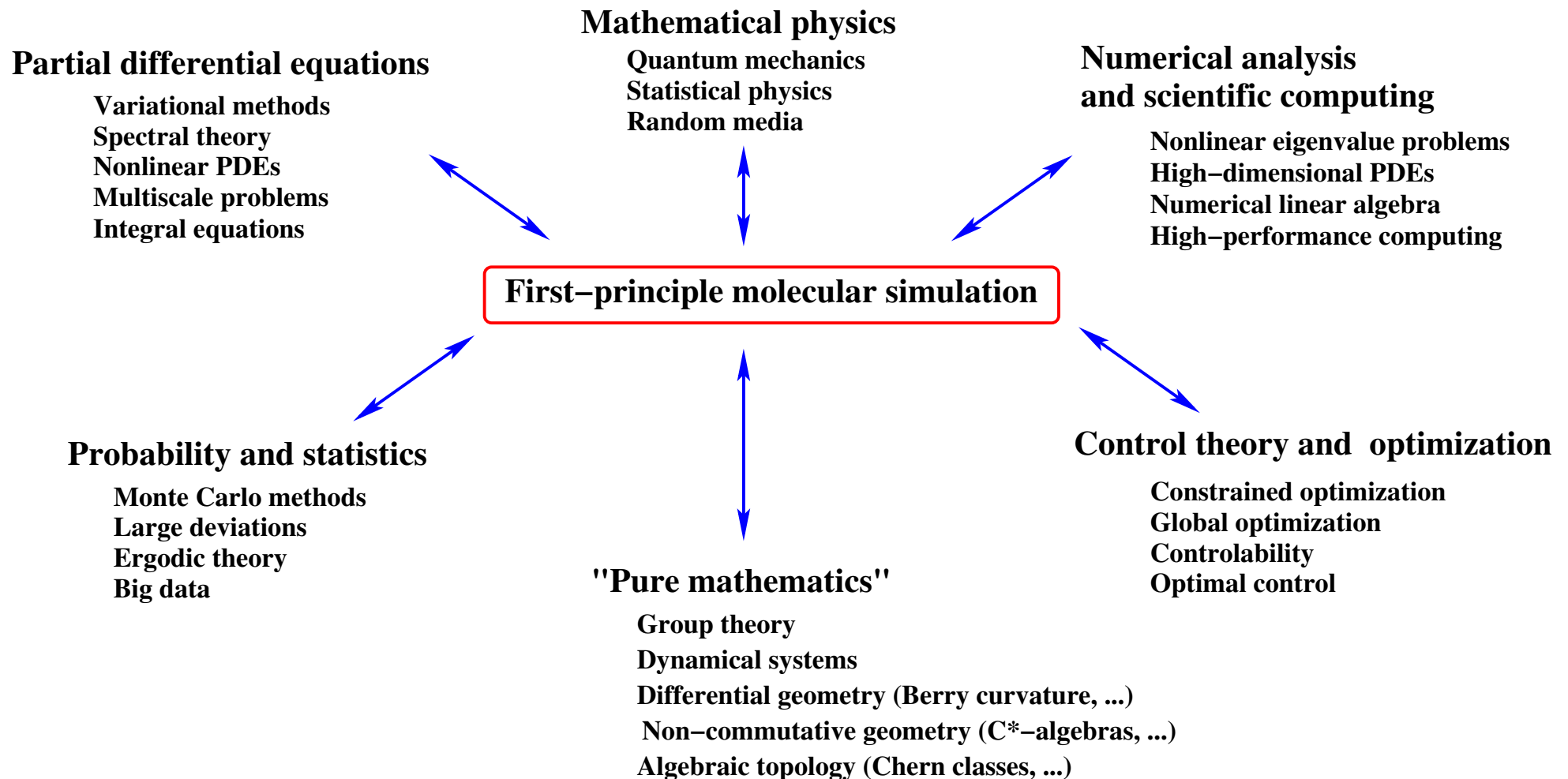
$$c \simeq 137.0359996287515\dots, \quad k_B = 3.16681537\dots \times 10^{-6}$$

- the charges and masses of the nuclei

$$z_H = 1, \quad z_O = 8, \quad m_H = 1836.152701\dots, \quad m_{16O} = 29156.944123\dots$$

In principle, it is therefore possible to compute all the properties of any molecular system from its chemical formula.

The mathematical analysis of first-principle simulation models and their numerical simulation are challenging tasks: depending on the model and on the system, various fields of pure and applied mathematics are involved!



Part I: modeling

1. The quantum many-body problem
2. First-principle molecular simulation
3. Density Functional Theory and Kohn-Sham models
4. Infinite systems

Part II: numerical methods

5. Standard discretization methods and algorithms
6. Advanced methods and current research

1 - The quantum many-body problem

First principles of (non-relativistic) quantum mechanics

An isolated quantum system is described by

- a state space \mathcal{H} (a complex Hilbert space);
- a Hamiltonian H (a self-adjoint operator on \mathcal{H});
- other observables (s.a. op. on \mathcal{H}) allowing to connect theory and exper.

The state of the system at time t is completely characterized by a **wavefunction** $\Psi(t) \in \mathcal{H}$ such that $\|\Psi(t)\|_{\mathcal{H}} = 1$.

Time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi}{dt}(t) = H\Psi(t)$$

Time-dependent Schrödinger equation

The steady states are of the form $\Psi(t) = f(t)\psi$, $f(t) \in \mathbb{C}$, $\psi \in \mathcal{H}$

$$H\psi = E\psi, \quad E \in \mathbb{R}, \quad \|\psi\|_{\mathcal{H}} = 1, \quad f(t) = e^{-iEt/\hbar}$$

Quantum mechanics for one-particle systems

Consider a particle of mass m subjected to an external potential V_{ext} :

- **state space:** $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C})$ (spin is omitted for simplicity);
- **Hamiltonian:** $H = -\frac{\hbar^2}{2m}\Delta + V_{\text{ext}}$ (self-adjoint operator on \mathcal{H}).

$|\Psi(t, \mathbf{r})|^2$: **probability density of observing the particle at point \mathbf{r} at time t**

$$\int_{\mathbb{R}^3} |\Psi(t, \mathbf{r})|^2 d\mathbf{r} = \|\Psi(t)\|_{\mathcal{H}}^2 = 1.$$

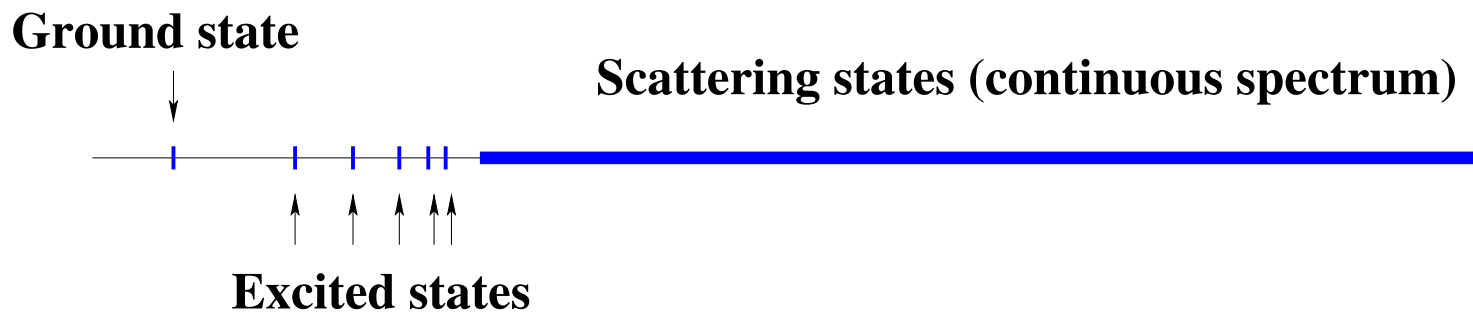
Time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi}{dt}(t) = H\Psi(t) \quad \longrightarrow \quad i\hbar \frac{\partial \Psi}{\partial t}(t, \mathbf{r}) = -\frac{\hbar^2}{2m} \Delta \Psi(t, \mathbf{r}) + V_{\text{ext}}(\mathbf{r})\Psi(t, \mathbf{r})$$

Time-independent Schrödinger equation

$$H\psi = E\psi \quad \longrightarrow \quad -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Typical spectrum of the Hamiltonian $H = -\frac{\hbar^2}{2m}\Delta + V_{\text{ext}}$ for 1 e⁻ systems



Ex.: $V_{\text{ext}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}$ (Hydrogen atom), $\sigma(H) = \left\{ -\frac{E_{\text{Ryd}}}{n^2} \right\}_{n \in \mathbb{N}^*} \cup [0, +\infty[.$

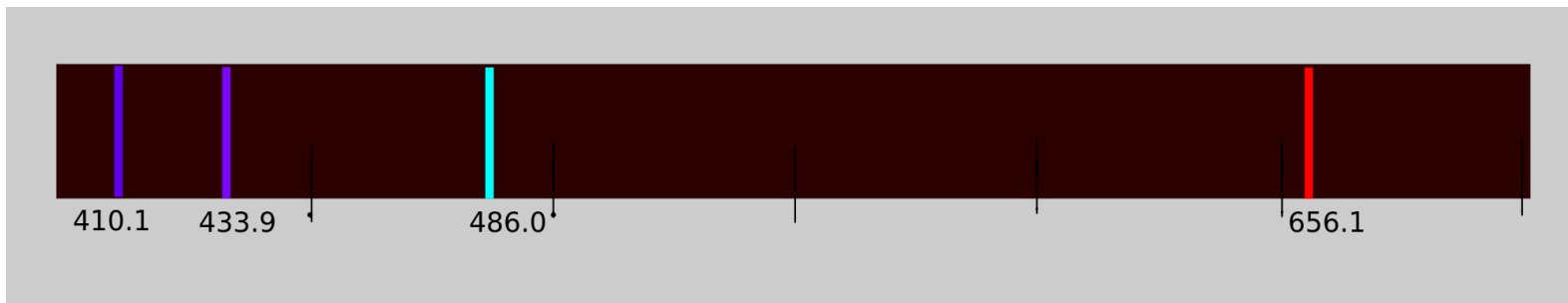
Physical meaning of the discrete energy levels

Example of the hydrogen atom

$$-\frac{\hbar^2}{2m_e}\Delta\Psi(x) - \frac{e^2}{4\pi\epsilon_0|x|}\Psi(x) = E\Psi(x)$$

$$E_n = -\frac{E_{\text{Ryd}}}{n^2}, \quad n \in \mathbb{N}^*, \quad E_{\text{Ryd}} = \frac{m_e}{2} \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2, \quad \lambda_{m \rightarrow n} = \frac{8\pi\hbar c}{E_{\text{Ryd}}} \left(\frac{1}{n^2} - \frac{1}{m^2} \right)^{-1}$$

Balmer series (nm): $\lambda_{6 \rightarrow 2} = 410.07$, $\lambda_{5 \rightarrow 2} = 433.94$, $\lambda_{4 \rightarrow 2} = 486.01$, $\lambda_{3 \rightarrow 2} = 656.11$
 $\lambda_{6 \rightarrow 2}^{\text{exp}} = 410.17$, $\lambda_{5 \rightarrow 2}^{\text{exp}} = 434.05$, $\lambda_{4 \rightarrow 2}^{\text{exp}} = 486.13$, $\lambda_{3 \rightarrow 2}^{\text{exp}} = 656.28$



On the physical meaning of point and continuous spectra

Theorem (RAGE, Ruelle '69, Amrein and Georgescu '73, Enss '78).

Let H be a locally compact self-adjoint operator on $L^2(\mathbb{R}^d)$.

[Ex.: the Hamiltonian of the hydrogen atom satisfies these assumptions.]

Let $\mathcal{H}_p = \overline{\text{Span}\{\text{eigenvectors of } H\}}$ and $\mathcal{H}_c = \mathcal{H}_p^\perp$.

[Ex.: for the Hamiltonian of the hydrogen atom, $\dim(\mathcal{H}_p) = \dim(\mathcal{H}_c) = \infty$.]

Let χ_{B_R} be the characteristic function of the ball $B_R = \{\mathbf{r} \in \mathbb{R}^d \mid |\mathbf{r}| < R\}$.

Then

$$(\phi_0 \in \mathcal{H}_p) \Leftrightarrow \forall \varepsilon > 0, \exists R > 0, \forall t \geq 0, \left\| (1 - \chi_{B_R}) e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 \leq \varepsilon;$$

$$(\phi_0 \in \mathcal{H}_c) \Leftrightarrow \forall R > 0, \lim_{T \rightarrow +\infty} \frac{1}{T} \int_0^T \left\| \chi_{B_R} e^{-itH/\hbar} \phi_0 \right\|_{L^2}^2 dt = 0.$$

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\mathcal{H}_p : set of bound states, \mathcal{H}_c : set of scattering states.

Quantum mechanics for two-particle systems

State space: $\mathcal{H} \subset L^2(\mathbb{R}^3, \mathbb{C}) \otimes L^2(\mathbb{R}^3, \mathbb{C}) \equiv L^2(\mathbb{R}^6, \mathbb{C})$

$|\Psi(t, \mathbf{r}_1, \mathbf{r}_2)|^2$: **probability density of observing at time t the particle 1 at \mathbf{r}_1 and the particle 2 at \mathbf{r}_2**

Symmetry constraints

- **two different particles:** $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \otimes L^2(\mathbb{R}^3, \mathbb{C})$

- **two identical bosons (e.g. two C^{12} nuclei):** $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \otimes_s L^2(\mathbb{R}^3, \mathbb{C})$

$$\Psi(t, \mathbf{r}_2, \mathbf{r}_1) = \Psi(t, \mathbf{r}_1, \mathbf{r}_2)$$

- **two identical fermions (e.g. two electrons):** $\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}) \wedge L^2(\mathbb{R}^3, \mathbb{C})$

$$\Psi(t, \mathbf{r}_2, \mathbf{r}_1) = -\Psi(t, \mathbf{r}_1, \mathbf{r}_2) \quad \text{(Pauli principle)}$$

density $\rho(t, \mathbf{r}) = \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}, \mathbf{r}_2)|^2 d\mathbf{r}_2 + \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}_1, \mathbf{r})|^2 d\mathbf{r}_1 = 2 \int_{\mathbb{R}^3} |\Psi(t, \mathbf{r}, \mathbf{r}_2)|^2 d\mathbf{r}_2$

Quantum mechanics for N -particle systems

Consider N particles of masses m_1, \dots, m_N subjected to an external potential $V_{\text{ext}}(\mathbf{r})$ and pair-interaction potentials $W_{ij}(\mathbf{r}_i, \mathbf{r}_j)$.

- **State space:** $\mathcal{H} \subset L^2(\mathbb{R}^3, \mathbb{C}) \otimes \dots \otimes L^2(\mathbb{R}^3, \mathbb{C}) \equiv L^2(\mathbb{R}^{3N}, \mathbb{C})$

$|\Psi(t, \mathbf{r}_1, \dots, \mathbf{r}_N)|^2$: probability density of observing at time t the particle 1 at \mathbf{r}_1 , the particle 2 at \mathbf{r}_2 , ...

- **Time-independent Schrödinger equation**

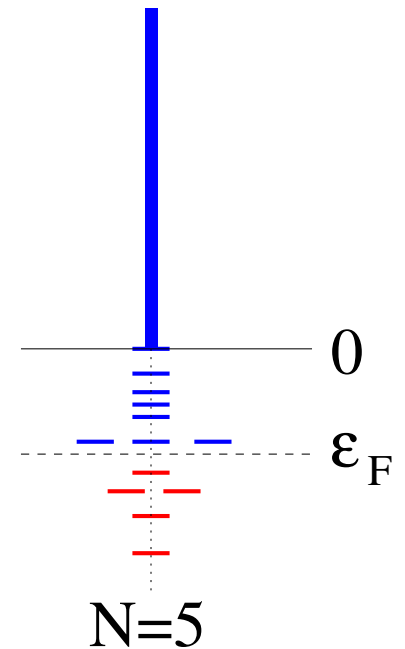
$$\left(- \sum_{i=1}^N \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} W_{ij}(\mathbf{r}_i, \mathbf{r}_j) \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

→ **3N-dimensional linear elliptic eigenvalue problem**

Ground state of N non-interacting identical particles of mass m subjected to an external potential $V_{\text{ext}}(\mathbf{r})$

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m} \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) = \sum_{i=1}^N \mathfrak{h}_{\mathbf{r}_i}$$

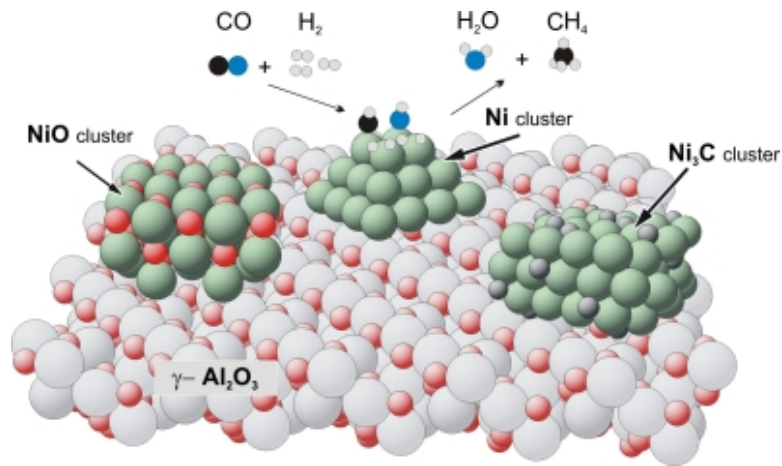
$$\left\{ \begin{array}{l} \mathfrak{h} \phi_i = \varepsilon_i \phi_i, \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \\ \mathfrak{h} = -\frac{\hbar^2}{2m} \Delta + V_{\text{ext}} \end{array} \right.$$



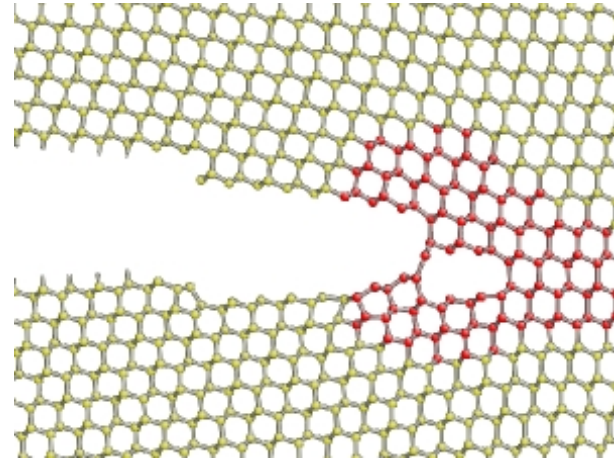
- **Bosonic ground state:** $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi_1(\mathbf{r}_i), \quad \rho(\mathbf{r}) = N|\phi_1(\mathbf{r})|^2$

- **Fermionic gr. st.:** $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \mathbf{det}(\phi_i(\mathbf{r}_j)), \quad \rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$

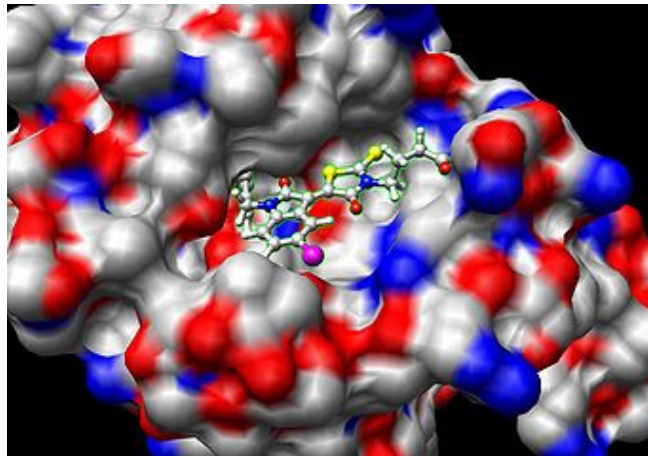
2 - First-principle molecular simulation



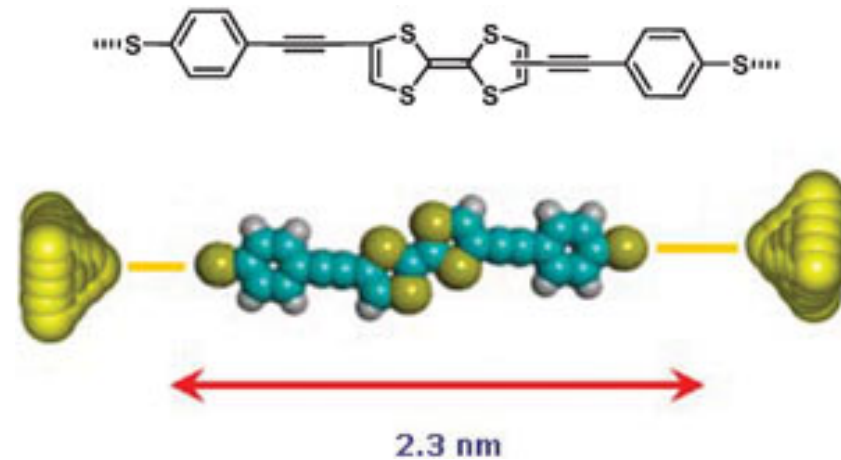
Chemistry



Materials science



Molecular biology



Nanotechnology

Key observation

- A molecule is a set of M nuclei and N electrons.
- The state space $\mathcal{H} \subset L^2(\mathbb{R}^{3(M+N)}, \mathbb{C})$ and the Hamiltonian of the molecule can be deduced from its chemical formula:

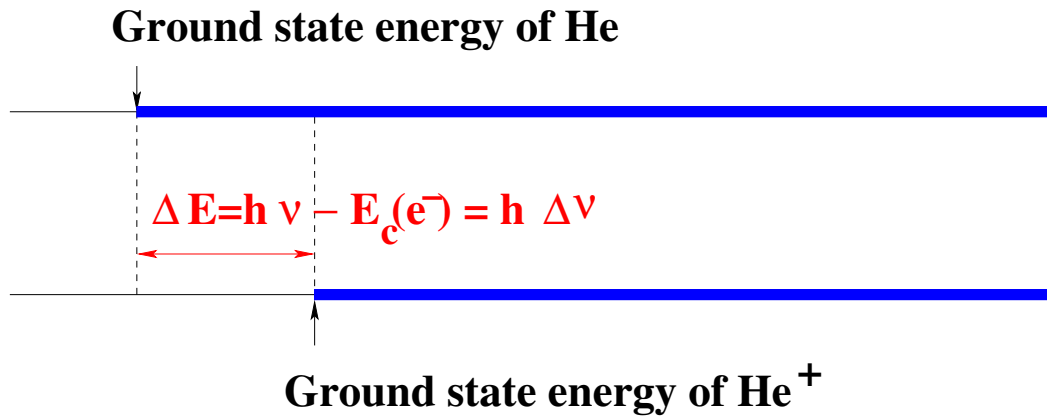
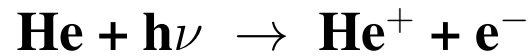
$$H = - \sum_{k=1}^M \frac{1}{2m_k} \Delta_{\mathbf{R}_k} - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$

Atomic units: $\hbar = 1$, $m_e = 1$, $e = 1$, $4\pi\epsilon_0 = 1$.

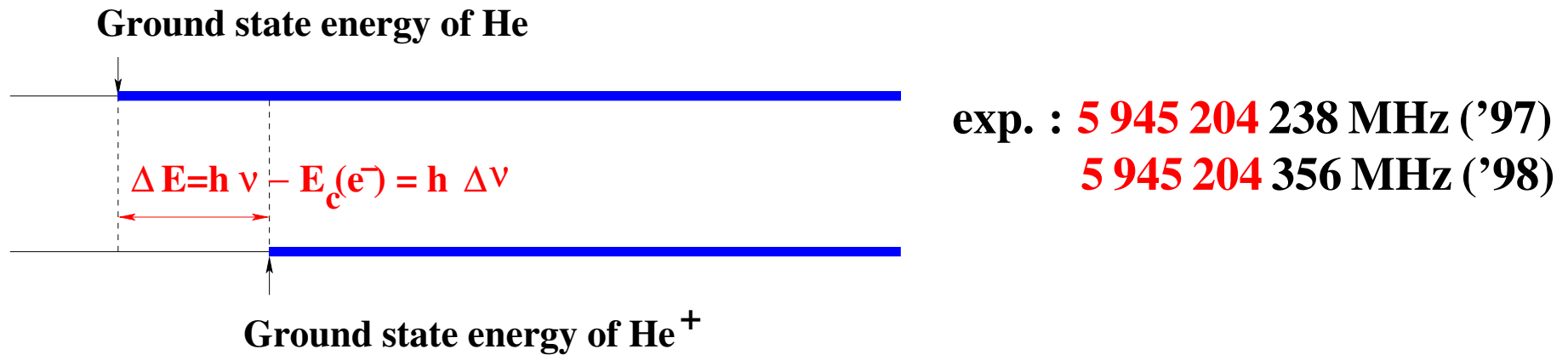
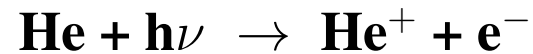
- This Hamiltonian is free of empirical parameters specific to the system.

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solved. (Dirac, 1929)

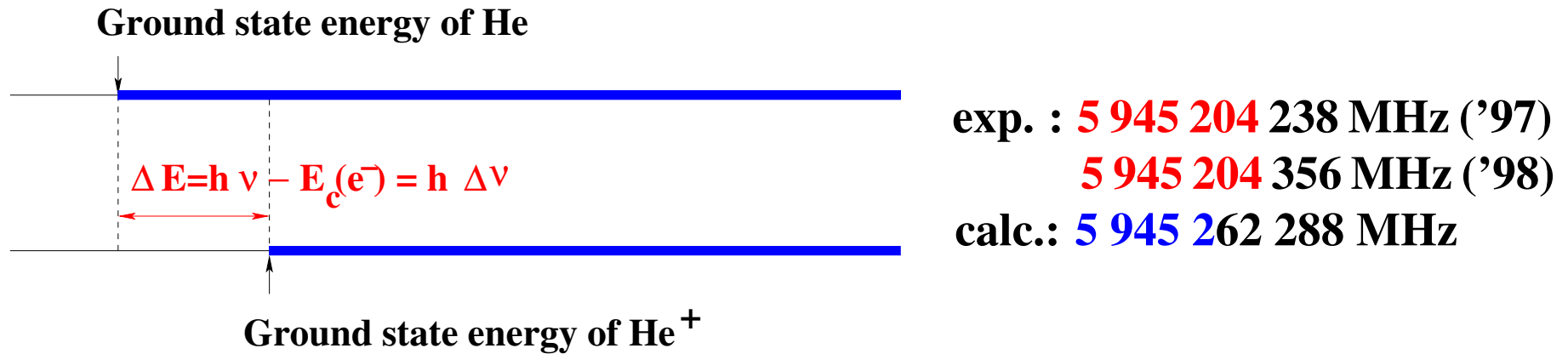
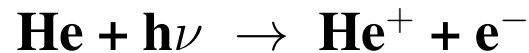
Ionization energy of Helium (Korobov & Yelkhovsky '01):



exp. : 5 945 204 238 MHz ('97)
 5 945 204 356 MHz ('98)

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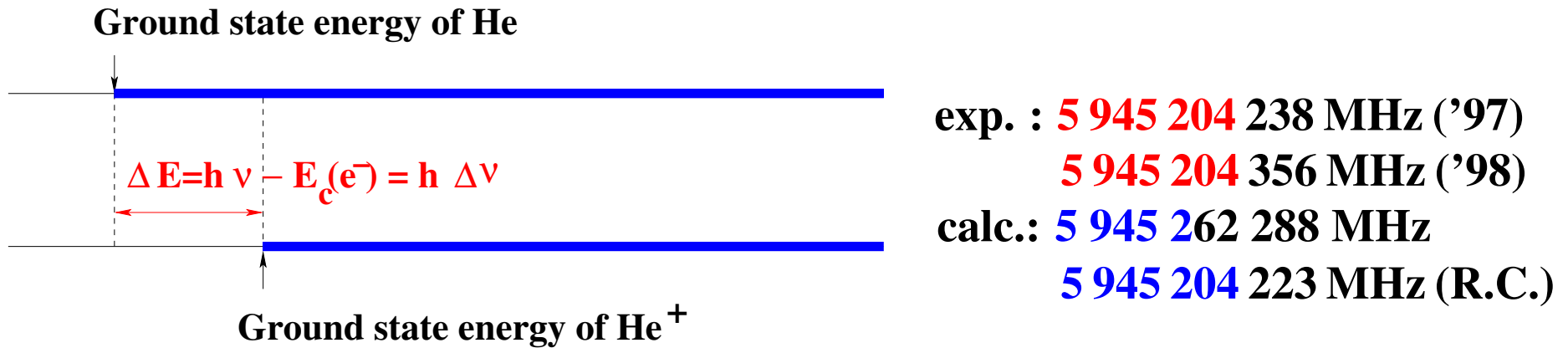
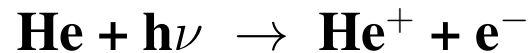
Ionization energy of Helium (Korobov & Yelkhovsky '01):



$$H_{\text{He}} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$H_{\text{He}^+} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|}, \quad m = 7294.29953 \dots \text{ a.u.}$$

Ionization energy of Helium (Korobov & Yelkhovsky '01):



$$H_{\text{He}} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \text{Breit terms}$$

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Example: computation of some properties of the water molecule (H₂O)

A water molecule consists of $M = 3$ atomic nuclei (1 oxygen + 2 hydrogens) and $N = 10$ electrons in Coulomb interaction.

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The only parameters of these models are

- a few fundamental constants of physics (atomic units)

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad \varepsilon_0 = (4\pi)^{-1},$$

$$c \simeq 137.0359996287515\dots, \quad k_B = 3.16681537\dots \times 10^{-6}$$

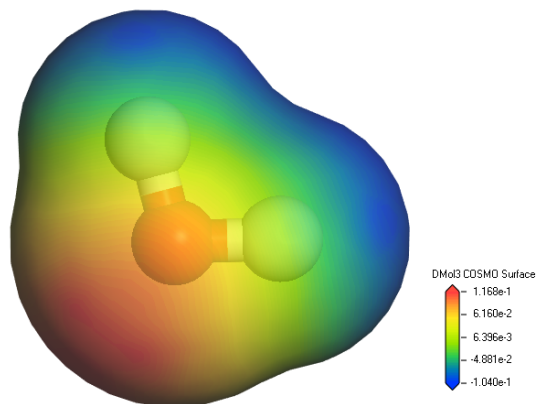
- the charges and masses of the hydrogen and oxygen (16) nuclei

$$z_H = 1, \quad z_O = 8, \quad m_H = 1836.152701\dots, \quad m_{16O} = 29156.944123\dots$$

Born-Oppenheimer strategy (based on the fact that $m_e/m_{\text{nuc}} \ll 1$):

- Step 1: definition of the potential energy surfaces (elec. struct. calc.)
- Step 2: analysis of the potential energy surfaces.

Electronic problem for a given nuclear configuration $\{\mathbf{R}_k\}_{1 \leq k \leq M}$



Ex: water molecule H_2O

$$M = 3, N = 10, z_1 = 8, z_2 = 1, z_3 = 1$$

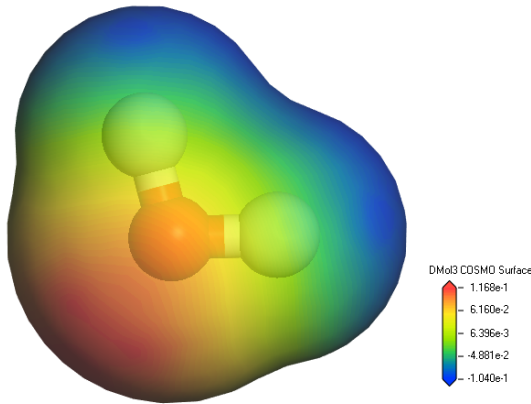
$$V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

$$\left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ probability density of observing electron 1 at \mathbf{r}_1 , electron 2 at \mathbf{r}_2 , ...

Warning: in this lecture, spin is omitted for simplicity

Electronic problem for a given nuclear configuration $\{\mathbf{R}_k\}_{1 \leq k \leq M}$



Ex: water molecule H_2O

$$M = 3, N = 10, z_1 = 8, z_2 = 1, z_3 = 1$$

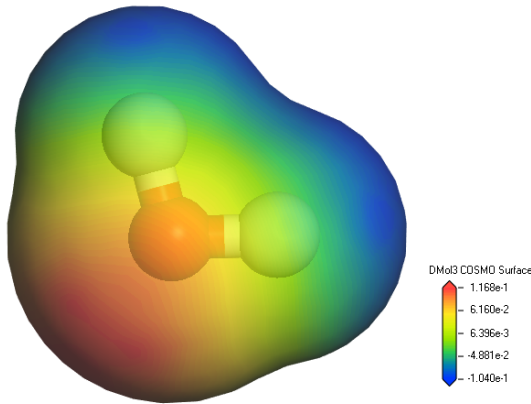
$$V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

$$\left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ **probability density of observing electron 1 at \mathbf{r}_1 , electron 2 at \mathbf{r}_2 , ...**

$$\forall p \in \mathfrak{S}_N, \quad \Psi(\mathbf{r}_{p(1)}, \dots, \mathbf{r}_{p(N)}) = \varepsilon(p) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad \textbf{(Pauli principle)}$$

Electronic problem for a given nuclear configuration $\{\mathbf{R}_k\}_{1 \leq k \leq M}$



Ex: water molecule H₂O

$$M = 3, N = 10, z_1 = 8, z_2 = 1, z_3 = 1$$

$$V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

$$\left(-\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ **probability density of observing electron 1 at \mathbf{r}_1 , electron 2 at \mathbf{r}_2 , ...**

$$\forall p \in \mathfrak{S}_N, \quad \Psi(\mathbf{r}_{p(1)}, \dots, \mathbf{r}_{p(N)}) = \varepsilon(p) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad \textbf{(Pauli principle)}$$

$$\|\Psi\|_{L^2} = 1, \quad \rho_{\Psi}(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N$$

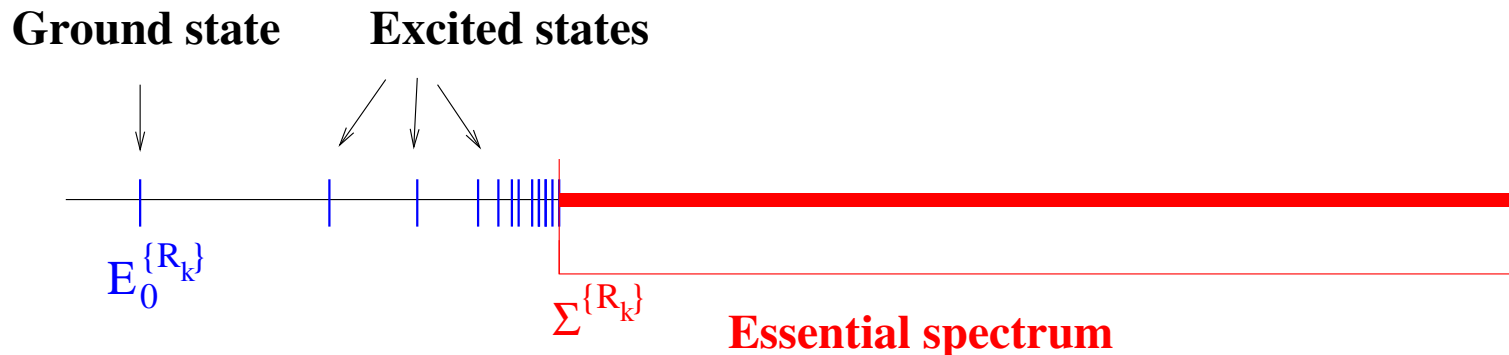
Spectrum of the electronic hamiltonian

$$H_N^{\{\mathbf{R}_k\}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^N V_{\{\mathbf{R}_k\}}^{\text{ne}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{on} \quad \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C})$$

(Pauli principle)

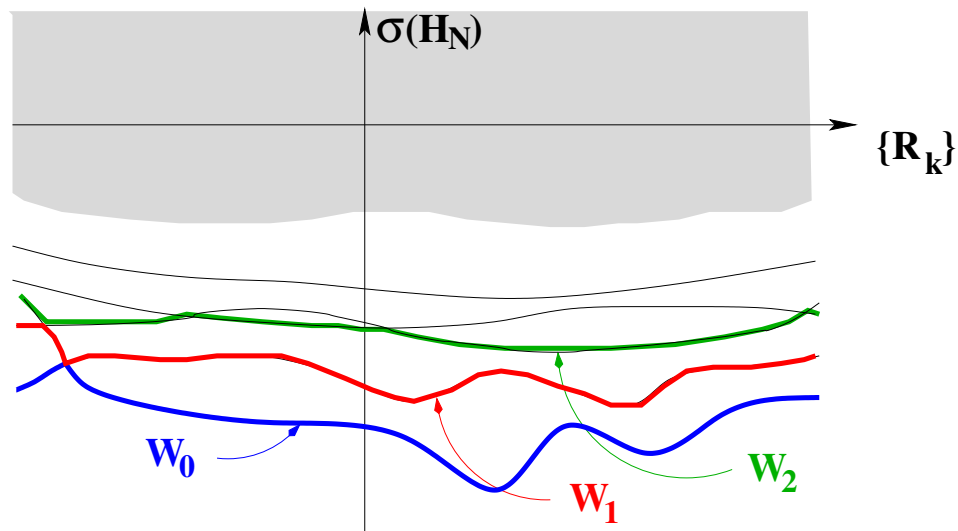
Zhislin's theorem: if $N \leq \sum_{k=1}^M z_k$ (neutral or positively charged system), then

$$\sigma(H_N^{\{\mathbf{R}_k\}}) = \left\{ E_0^{\{\mathbf{R}_k\}} \leq E_1^{\{\mathbf{R}_k\}} \leq E_2^{\{\mathbf{R}_k\}} \dots \right\} \cup [\Sigma^{\{\mathbf{R}_k\}}, +\infty).$$



Step 1: definition of the potential energy surfaces

$$W_n(\mathbf{R}_1, \dots, \mathbf{R}_M) = E_n^{\{\mathbf{R}_k\}} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$



Step 2: analysis of the potential energy surfaces

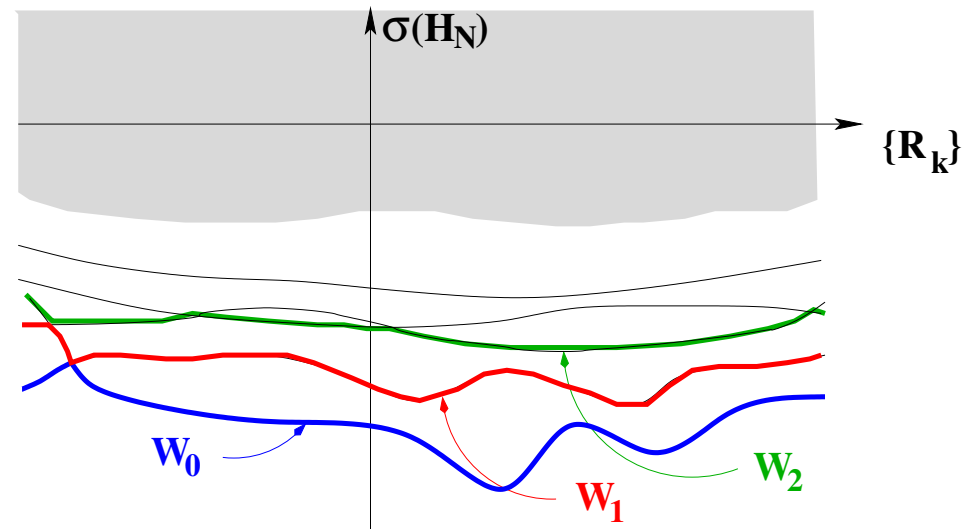
Born-Oppenheimer approximation

- adiabatic approximation

$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$



Step 2: analysis of the potential energy surfaces

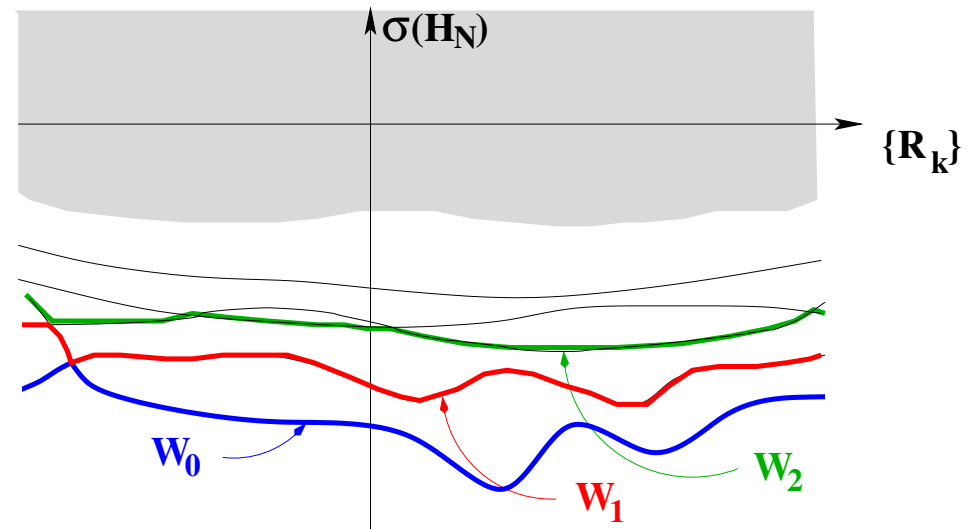
Born-Oppenheimer approximation

- adiabatic approximation

$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$



First-principle molecular dynamics

$$m_k \frac{d^2 \mathbf{R}_k}{dt^2}(t) = -\nabla_{\mathbf{R}_k} W_0(\mathbf{R}_1(t), \dots, \mathbf{R}_M(t)), \quad 1 \leq k \leq M$$

The nuclei behave as point-like classical particle interacting via the effective M -body potential W_0 .

Step 2: analysis of the potential energy surfaces

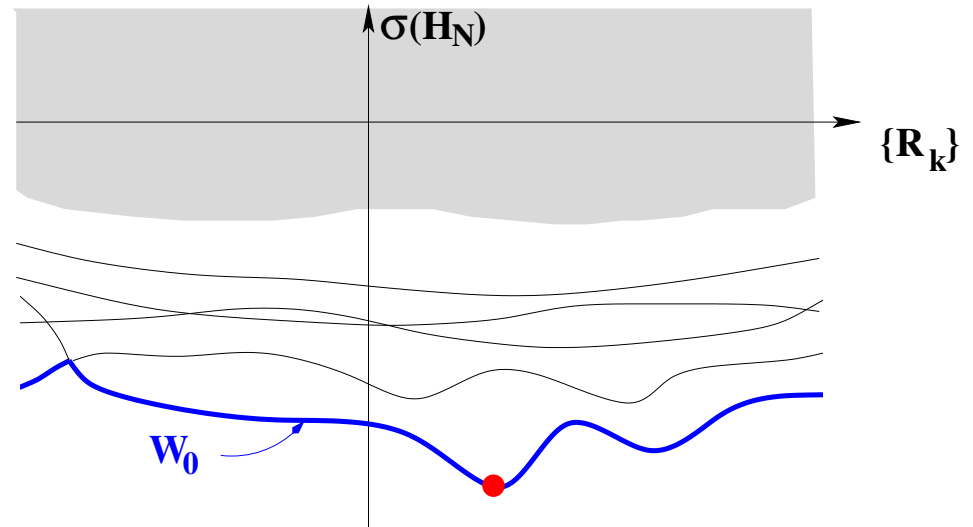
Born-Oppenheimer approximation

- adiabatic approximation

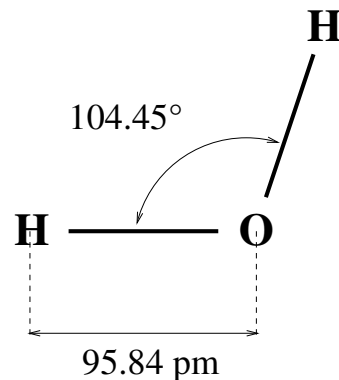
$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$



Global minima of W_0 : equilibrium configurations of the system



Step 2: analysis of the potential energy surfaces

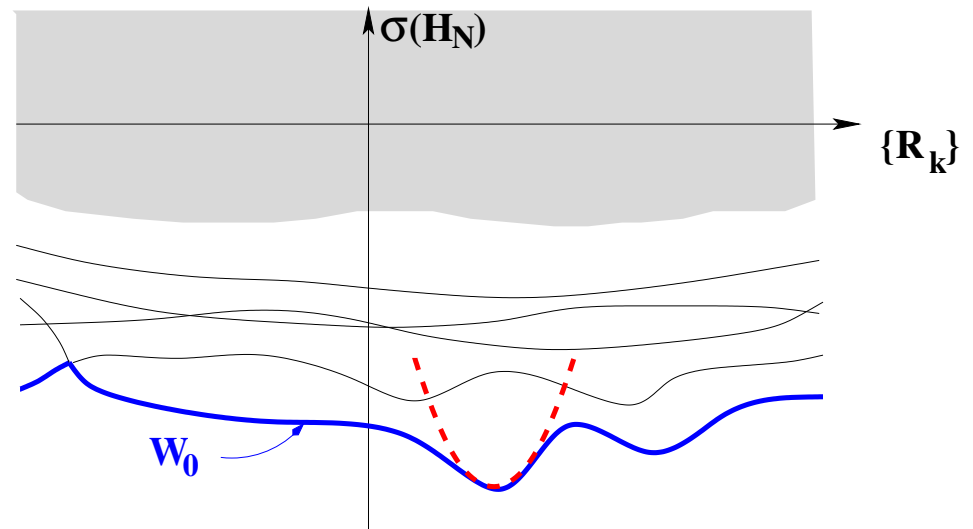
Born-Oppenheimer approximation

- adiabatic approximation

$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$



Vibration frequencies (harm. approx.)

$$\mathbf{R}_k(t) = \mathbf{R}_k^0 + \mathbf{y}_k(t)$$

$$m_k \frac{d^2 y_{k,i}}{dt^2} = - \sum_{l=1}^M \sum_{j=1}^3 \frac{\partial^2 W_0}{\partial R_{k,i} \partial R_{l,j}}(\mathbf{R}_0) y_{l,j}$$

Step 2: analysis of the potential energy surfaces

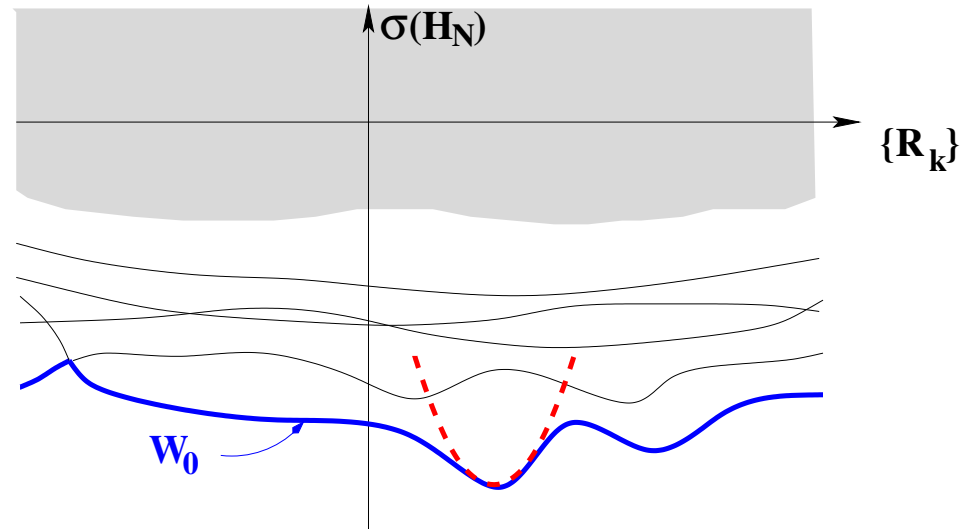
Born-Oppenheimer approximation

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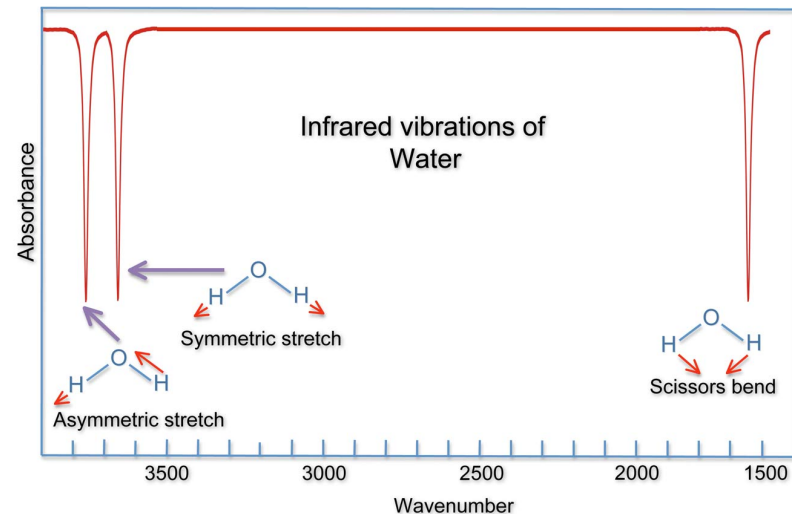


Vibration frequencies (harm. approx.)

$$\mathbf{R}_k(t) = \mathbf{R}_k^0 + \mathbf{y}_k(t)$$

$$m_k \frac{d^2 y_{k,i}}{dt^2} = - \sum_{l=1}^M \sum_{j=1}^3 \frac{\partial^2 W_0}{\partial R_{k,i} \partial R_{l,j}} (\mathbf{R}_0) y_{l,j}$$

→ infrared spectrum



Step 2: analysis of the potential energy surfaces

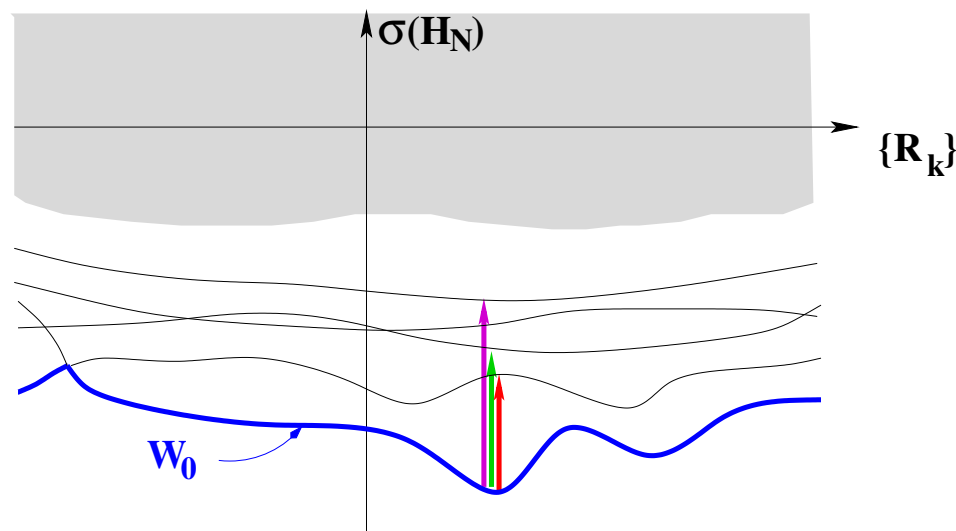
Born-Oppenheimer approximation

- adiabatic approximation

$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$



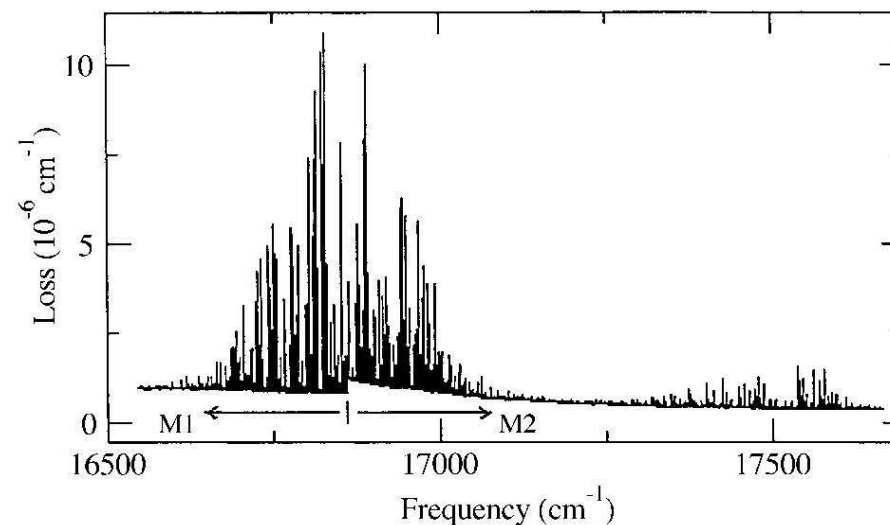
Vertical transition energies:

visible spectrum (color)

ultraviolet spectrum

X spectrum

ionization energy



Step 2: analysis of the potential energy surfaces

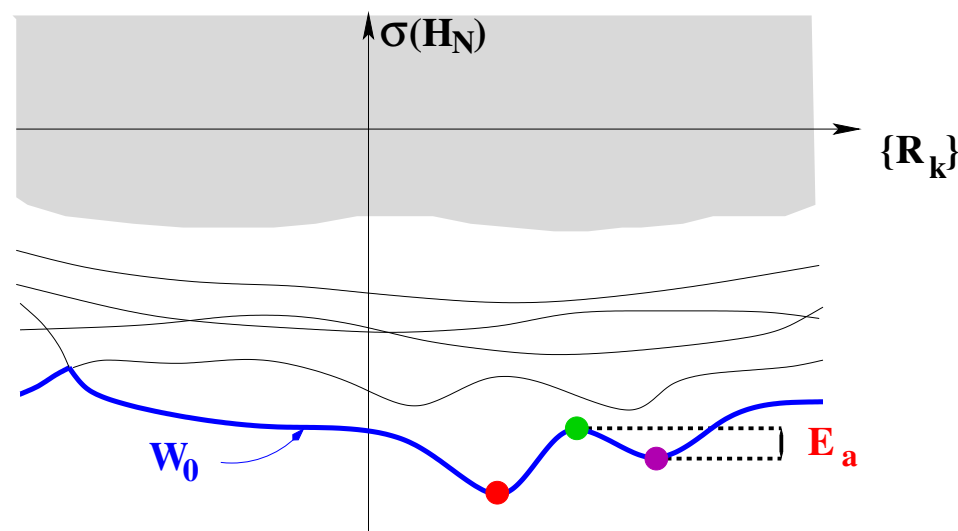
Born-Oppenheimer approximation

- adiabatic approximation

$$m_e/m_{\text{nuc}} \ll 1$$

- semiclassical approximation

on the nuclear dynamics: $\hbar \rightarrow 0$

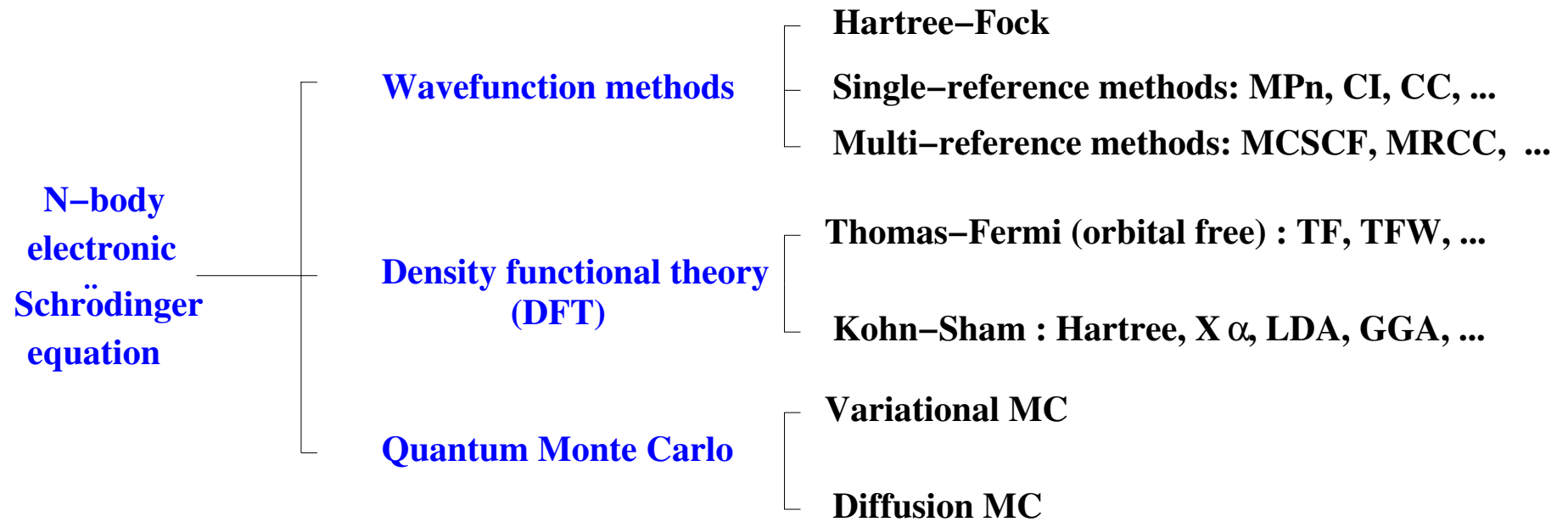


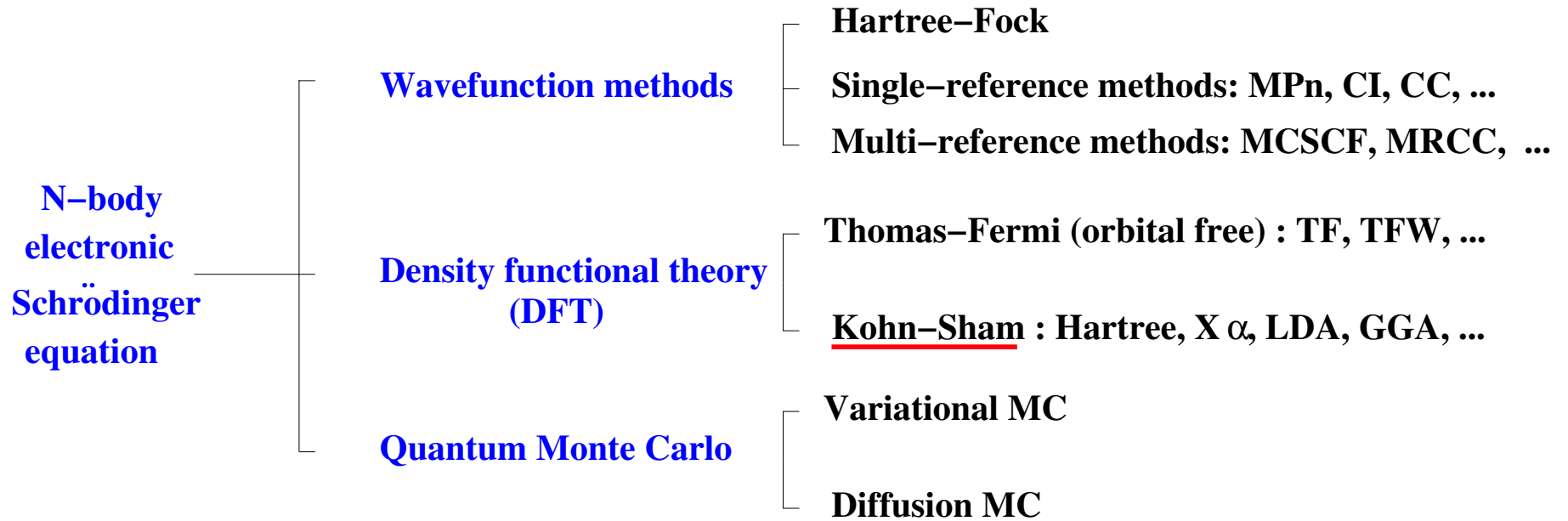
Local minima: (meta)stable states (reactants and products)

Critical points of W_0 with Morse index 1: transition states



$$k_{\text{TST}} = \frac{\prod_{i=1}^{3N-6} \nu_i^{\text{Re}}}{\prod_{i=1}^{3N-7} \nu_i^{\text{TS},+}} e^{-E_a/k_B T} \quad (\text{large deviation theory}).$$

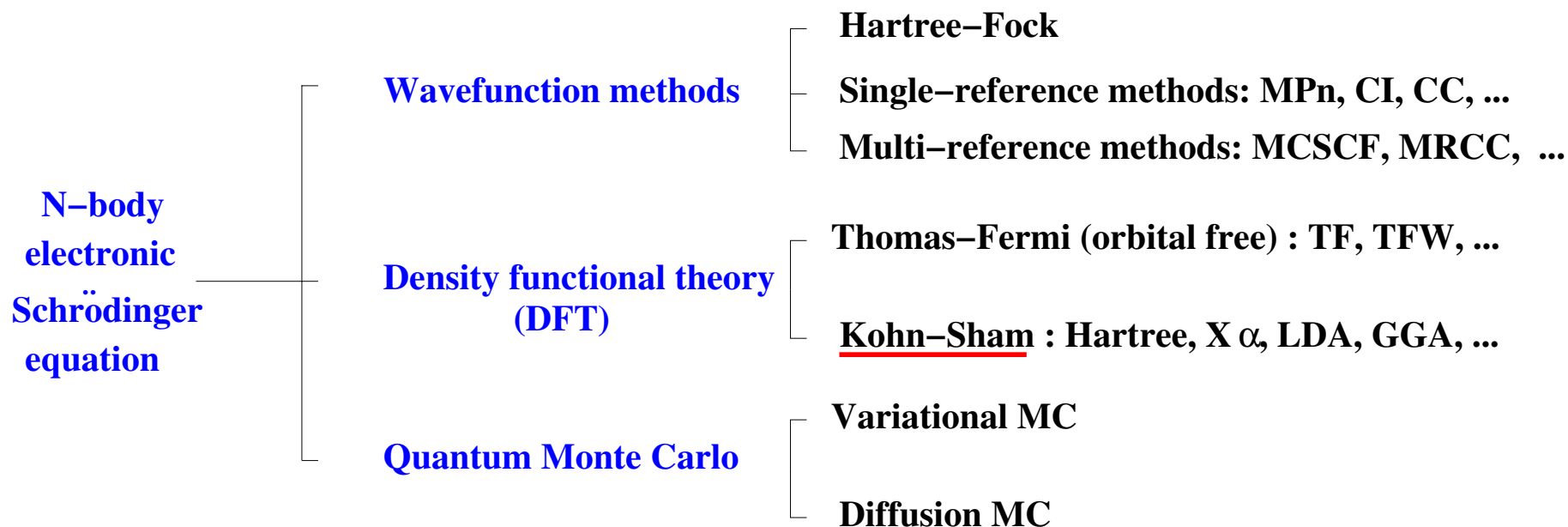




Kohn-Sham model

$$\left(-\frac{1}{2}\Delta + V_{\{\mathbf{R}_k\}}^{\text{KS}}[\phi_1, \dots, \phi_N] \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad 1 \leq i, j \leq N$$

→ **system of N nonlinear 3D Schrödinger equations**

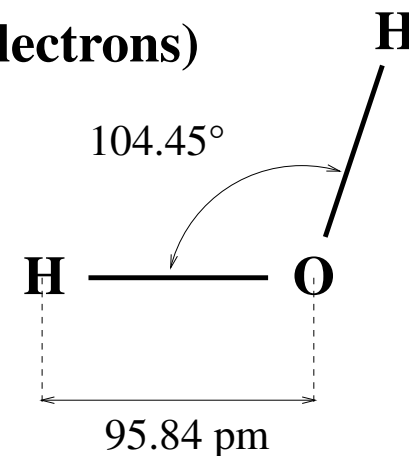


Equilibrium geometry of the water molecule (3 nuclei, 10 electrons)

Minimizers of $W_0(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = w_0(r_{\text{OH}_1}, r_{\text{OH}_2}, \theta_{\text{HOH}})$

Kohn-Sham DFT calculation (scales as N^3 or less)

GGA (PBE)-6-311+G**: 96.90 pm, 104.75°



3 - Density Functional Theory and Kohn-Sham models

Hohenberg-Kohn splitting of the electronic Hamiltonian

$$E_0 = \inf \{ \langle \Psi | H_N | \Psi \rangle, \Psi \in \mathcal{W}_N \}, \quad \mathcal{W}_N = \left\{ \Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3) \cap H^1(\mathbb{R}^{3N}), \|\Psi\|_{L^2} = 1 \right\}$$

$$H_N = H_N^1 + V_{\text{ne}} = H_N^1 + \sum_{i=1}^N V(\mathbf{r}_i)$$

$$H_N^1 = T + V_{\text{ee}} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

Electronic density

$$\Psi \in \mathcal{W}_N \quad \mapsto \quad \rho_\Psi(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

Levy constrained search approach

$$\begin{aligned}
 E_0 &= \inf_{\Psi} \langle \Psi | H_N | \Psi \rangle \\
 &= \inf_{\Psi} \left(\langle \Psi | H_N^1 | \Psi \rangle + \langle \Psi | \left(\sum_{i=1}^N V(\mathbf{r}_i) \right) | \Psi \rangle \right) \\
 &= \inf_{\Psi} \left(\langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_{\Psi} V \right) \\
 &= \inf_{\rho} \inf_{\Psi | \rho_{\Psi} = \rho} \left(\langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho_{\Psi} V \right) \\
 &= \inf_{\rho} \left(\inf_{\Psi | \rho_{\Psi} = \rho} \langle \Psi | H_N^1 | \Psi \rangle + \int_{\mathbb{R}^3} \rho V \right) \\
 &= \inf_{\rho} \left(F_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V \right)
 \end{aligned}$$

Levy-Lieb functional

$$E_0 = \inf \left\{ F_{\text{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V, \rho \in \mathcal{R}_N \right\}$$

$$F_{\text{LL}}(\rho) = \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle, \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\}$$

$$\mathcal{R}_N = \left\{ \rho, \exists \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \right\} = \left\{ \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}$$

$F_{\text{LL}}(\rho)$ is a “universal” functional of the density

Problem: no easy-to-compute expression of $F_{\text{LL}}(\rho)$ is known

Lieb functional

For any $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, we can define

$$E(v) = \inf \left\{ \langle \Psi | H_N^1 + \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle, \Psi \in \mathcal{W}_N \right\}$$

and $v \mapsto E(v)$ is a real-valued, concave, continuous function.

It holds (Lieb '83)

$$E(v) = \inf \left\{ F_L(\rho) + \int_{\mathbb{R}^3} \rho v, \rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \right\}$$

where $F_L(\rho)$ is the convex w-l.s.c. function defined on $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$ by

$$F_L(\rho) = \sup \left\{ E(v) - \int_{\mathbb{R}^3} \rho v, v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \right\}.$$

No explicit expressions of the functionals F_L and F_{LL} are known.

Approximations are needed for numerical simulations.

Two classes of approximate functionals are available, built from the exact functionals of simple reference systems:

- **orbital-free models**: reference system = homogeneous electron gas
orbital-free functionals are cheap but inaccurate except in a few cases;
- **Kohn-Sham models**: reference system = N non-interacting electrons
Kohn-Sham functionals are much more accurate, but more expensive.

In orbital-free models, the density functional is explicit in ρ .

Examples:

- **Thomas-Fermi (TF) model**

$$\mathcal{E}^{\text{TF}}(\rho) = C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \int_{\mathbb{R}^3} \rho V + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_0 \sim \inf \left\{ \mathcal{E}^{\text{TF}}(\rho), \rho \geq 0, \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}.$$

- **Thomas-Fermi-von Weizsäcker (TFW) model**

$$\mathcal{E}^{\text{TFW}}(\rho) = C_{\text{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + C_{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \int_{\mathbb{R}^3} \rho V + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_0 \sim \inf \left\{ \mathcal{E}^{\text{TFW}}(\rho), \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho = N \right\}.$$

Density functional theory for non-interacting electrons

	Hamiltonian	Levy-Lieb	Lieb
Interacting e⁻	H_N^1	$F_{LL}(\rho)$	$F_L(\rho)$
Non-interacting e⁻	H_N^0	$T_{LL}(\rho)$	$T_J(\rho)$

$$H_N^1 = T + V_{ee} = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad H_N^0 = T = - \sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i}$$

Levy-Lieb approach

$$\begin{aligned}
 T_{\text{LL}}(\rho) &= \inf \{ \langle \Psi | T | \Psi \rangle, \Psi \in \mathcal{W}_N \text{ s.t. } \rho_\Psi = \rho \} \\
 &\leq \inf \{ \langle \Psi | T | \Psi \rangle, \Psi \text{ is a Slater determinant s.t. } \rho_\Psi = \rho \} \\
 &= \inf \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \sum_{i=1}^N |\phi_i|^2 = \rho \right\} \\
 &= T_{\text{KS}}(\rho).
 \end{aligned}$$

A Slater determinant (with finite energy) is a wavefunction Ψ of the form

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \phi_N(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}, \quad \phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}.$$

Kohn-Sham model

1. For N *non interacting* electrons, the density functional is (approximatively) given by

$$T_{\text{KS}}(\rho) = \left\{ \sum_{i=1}^N \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3) \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \sum_{i=1}^N |\phi_i|^2 = \rho \right\}.$$

2. For a classical charge distribution of density ρ , the Coulomb interaction reads

$$J(\rho) \stackrel{\text{def}}{=} \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x - y|} dx dy.$$

3. Kohn and Sham proposed the following decomposition of F_{LL}

$$F_{\text{LL}}(\rho) = T_{\text{KS}}(\rho) + J(\rho) + E_{\text{xc}}(\rho) \quad \text{where} \quad E_{\text{xc}}(\rho) \stackrel{\text{def}}{=} F_{\text{LL}}(\rho) - T_{\text{KS}}(\rho) - J(\rho).$$

E_{xc} is called the **exchange-correlation functional**.

Exchange-correlation functional

$$|E_{\text{xc}}(\rho)| \ll J(\rho) \text{ and } T_{\text{KS}}(\rho).$$

A possible approximation of $E_{\text{xc}}(\rho)$ is

$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} e_{\text{xc}}(\rho(x)) dx$$

where $e_{\text{xc}}(\bar{\rho})$ is the exchange-correlation energy density in a homogeneous electron gas of density $\bar{\rho}$.

→ **Local Density Approximation (LDA)**

The function $e_{\text{xc}} : \mathbb{R}_+ \rightarrow \mathbb{R}$ is obtained by interpolation of asymptotic expansions and benchmark Quantum Monte Carlo calculations on the homogeneous electron gas.

Rewriting the minimization problem in terms of $\Phi = (\phi_1, \dots, \phi_N)$, one obtains

$$E_0 \simeq \inf \left\{ E^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\begin{aligned} E^{\text{KS}}(\Phi) = & \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V \\ & + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_{\Phi}(\mathbf{r})) d\mathbf{r} \end{aligned}$$

with

$$V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2.$$

Existence of solutions for neutral and positively charged systems: Le Bris '93, Anantharaman-Cancès '09.

Kohn-Sham equations (Euler-Lagrange + invariance + loc. min.)

$$\begin{cases} -\frac{1}{2}\Delta\phi_i + \mathcal{W}_\Phi\phi_i = \varepsilon_i\phi_i & 1 \leq i \leq N \\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} & 1 \leq i, j \leq N. \end{cases}$$

- In the Hartree-Fock model, the potential \mathcal{W}_Φ is nonlocal

$$\mathcal{W}_\Phi^{\text{HF}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\cdot|} \right) \phi - \int_{\mathbb{R}^3} \frac{\gamma_\Phi(\cdot, \mathbf{r}')}{|\cdot - \mathbf{r}'|} \phi(\mathbf{r}') d\mathbf{r}', \quad \gamma_\Phi(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$$

while it is local in the Kohn-Sham LDA model

$$\mathcal{W}_\Phi^{\text{KS-LDA}}\phi = \left(V + \rho_\Phi \star \frac{1}{|\cdot|} + \frac{de_{\text{xc}}}{d\rho}(\rho_\Phi) \right) \phi.$$

- In the Hartree-Fock model, $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$ are the lowest N eigenvalues of $-\frac{1}{2}\Delta + \mathcal{W}_\Phi$, while it is not known whether this property holds true for the Kohn-Sham LDA model.

"Improvements" of the LDA: Jacob's ladder (Perdew)

Heaven	Exact exchange–correlation functional
Rung 5	<p>explicit functionals of the Kohn-Sham occupied and unoccupied orbitals</p> <p>SAOP, ...</p>
Rung 4	<p>explicit functionals of the KS density matrix (ex: hybrid functionals)</p> <p>1/2 & 1/2, B3P, B3LYP, PBE0, O3LYP, X3LYP, mPW1PW91, BMK, PWB6K, B1B95, PW6B95, TPSSh, M05, ...</p>
Rung 3	<p>meta-GGA (explicit in $\rho(\mathbf{r})$, $\nabla\rho(\mathbf{r})$, $\Delta\rho(\mathbf{r})$ and $\tau(\mathbf{r}) = \sum_{i=1}^N \nabla\phi_i(\mathbf{r}) ^2$)</p> <p>BR89, tauPBE, VSXC, BB95, TPSS, PBS00, LAP, ...</p>
Rung 2	<p>GGA (explicit in $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$)</p> <p>SIC, PW91, BLYP, mPWPW91, PBE, revPBE, G96LYP, HCTH, OPTX, EDF1, ...</p>
Rung 1	<p>LDA (explicit in $\rho(\mathbf{r})$)</p>
Earth	Hartree (reduced Hartree–Fock) model

Physical interpretation of $F_L(\rho)$

Mixed states of N -electron systems are described by N -electron density matrices of the form

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle \langle \Psi_n|, \quad \Psi_n \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3), \quad \langle \Psi_m | \Psi_n \rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1$$

the density of Γ being given by

$$\rho_\Gamma(\mathbf{r}) = \sum_{n=1}^{+\infty} p_n \rho_{\Psi_n}(\mathbf{r}).$$

Γ is of finite energy if $\sum_{n=1}^{+\infty} p_n \|\nabla \Psi_n\|_{L^2}^2 < \infty$, its energy being then

$$\mathbf{Tr}(H_N \Gamma) = \sum_{n=1}^{+\infty} p_n \langle \Psi_n | H_N | \Psi_n \rangle = \mathbf{Tr}(H_N^1 \Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V.$$

Let us denote by \mathcal{D}_N the convex set consisting of the N -electron density matrices of finite energy

$$\{\rho \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho\} = \mathcal{R}_N.$$

Therefore

$$\begin{aligned} E_0 &= \inf \{ \mathbf{Tr} (H_N \Gamma), \Gamma \in \mathcal{D}_N \} \\ &= \inf \left\{ \mathbf{Tr} (H_N^1 \Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V, \Gamma \in \mathcal{D}_N \right\} \\ &= \inf \left\{ \inf \{ \mathbf{Tr} (H_N^1 \Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} + \int_{\mathbb{R}^3} \rho V, \rho \in \mathcal{R}_N \right\}. \end{aligned}$$

It holds that $F_L(\rho) = \begin{cases} \inf \{ \mathbf{Tr} (H_N^1 \Gamma), \Gamma \in \mathcal{D}_N, \rho_\Gamma = \rho \} & \text{if } \rho \in \mathcal{R}_N, \\ +\infty & \text{if } \rho \notin \mathcal{R}_N, \end{cases}$
and that F_L is the convex hull of F_{LL} on the convex set \mathcal{R}_N .

One-body reduced density matrices

Let $\Psi \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3)$ such that $\|\Psi\|_{L^2} = 1$. The (one-body) reduced density matrix associated with Ψ is the function

$$\gamma_{\Psi}(\mathbf{r}, \mathbf{r}') := N \int_{\mathbb{R}^{3(N-1)}} \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N.$$

Note that $\rho_{\Psi}(\mathbf{r}) = \gamma_{\Psi}(\mathbf{r}, \mathbf{r})$.

The function $\gamma_{\Psi}(\mathbf{r}, \mathbf{r}')$ can be considered as the Green kernel of the operator on $L^2(\mathbb{R}^3)$, also denoted by γ_{Ψ} , and called the one-body reduced density operator, defined for all $\phi \in L^2(\mathbb{R}^3)$ by

$$(\gamma_{\Psi}\phi)(\mathbf{r}) = \int_{\mathbb{R}^3} \gamma_{\Psi}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') d\mathbf{r}'.$$

The operator γ_Ψ is self-adjoint on $L^2(\mathbb{R}^3)$ and satisfies

$$0 \leq \gamma_\Psi \leq 1 \quad \text{and} \quad \text{Tr}(\gamma_\Psi) = N.$$

Therefore, γ_Ψ can be diagonalized as follows: there exists an orthonormal basis $(\phi_i)_{i \geq 1}$ of $L^2(\mathbb{R}^3)$ and a non-increasing sequence $(n_i)_{i \geq 1}$ of real numbers such that

$$\gamma_\Psi = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle \langle \phi_i| \quad \text{with} \quad 0 \leq n_i \leq 1 \quad \text{and} \quad \sum_{i=1}^{+\infty} n_i = N$$

The n_i and the ϕ_i are called respectively the natural occupation numbers and the natural spin-orbitals of the wavefunction Ψ .

If in addition Ψ is of finite energy, then all the ϕ_i are in $H^1(\mathbb{R}^3)$ and

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2} \sum_{i=1}^{+\infty} n_i \int_{\mathbb{R}^3} |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} = \text{Tr} \left(-\frac{1}{2} \Delta \gamma_\Psi \right).$$

Let $\Gamma \in \mathcal{D}_N$

$$\Gamma = \sum_{n=1}^{+\infty} p_n |\Psi_n\rangle\langle\Psi_n|, \quad \Psi_n \in \bigwedge_{i=1}^N L^2(\mathbb{R}^3), \quad \langle\Psi_m|\Psi_n\rangle = \delta_{mn}, \quad 0 \leq p_n \leq 1, \quad \sum_{n=1}^{+\infty} p_n = 1.$$

The first order reduced density operator associated with Γ is

$$\gamma_\Gamma = \sum_{n=1}^{+\infty} p_n \gamma_{\Psi_n}. \quad \text{Note that } \rho_\Gamma(\mathbf{r}) = \gamma_\Gamma(\mathbf{r}, \mathbf{r}).$$

It holds

$$\gamma_\Gamma^* = \gamma_\Gamma, \quad 0 \leq \gamma_\Gamma \leq 1, \quad \mathbf{Tr}(\gamma_\Gamma) = N, \quad \mathbf{Tr}(H_N^0 \Gamma) = \mathbf{Tr}\left(-\frac{1}{2}\Delta \gamma_\Gamma\right).$$

Ensemble N -representability of first-order reduced density matrices

$$\begin{aligned} \mathcal{C}_N &= \{\gamma \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \gamma_\Gamma = \gamma\} \\ &= \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1, \mathbf{Tr}(\gamma) = N, \mathbf{Tr}(-\Delta \gamma) < \infty\}. \end{aligned}$$

Lieb approach (Janak functional)

$$\begin{aligned}
 T_J(\rho) &= \inf \left\{ \mathbf{Tr}(H_N^0 \Gamma), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
 &= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma_\Gamma \right), \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho \right\} \\
 &= \inf \left\{ \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right), \gamma \in \mathcal{C}_N \text{ s.t. } \rho_\gamma = \rho \right\} \quad \text{where } \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}) \\
 &= \inf \left\{ \sum_{i=1}^{+\infty} \frac{1}{2} n_i \int_{\mathbb{R}^3} |\nabla \phi_i|^2, \phi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \right. \\
 &\quad \left. 0 \leq n_i \leq 1, \sum_{i=1}^{+\infty} n_i |\phi_i|^2 = \rho \right\}.
 \end{aligned}$$

Extended Kohn-Sham LDA model

$$\inf \{ \mathcal{E}(\gamma), \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)), 0 \leq \gamma \leq 1, \mathbf{Tr}(\gamma) = N, \mathbf{Tr}(-\Delta\gamma) < \infty \}$$

$$\mathcal{E}(\gamma) = \mathbf{Tr} \left(-\frac{1}{2} \Delta \gamma \right) + \int_{\mathbb{R}^3} \rho_\gamma V + J(\rho_\gamma) + \int_{\mathbb{R}^3} e_{\text{xc}}(\rho_\gamma), \quad \rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r}).$$

The minimization set \mathcal{C}_N is convex and any $\gamma \in \mathcal{C}_N$ can be written as

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle \langle \phi_i|$$

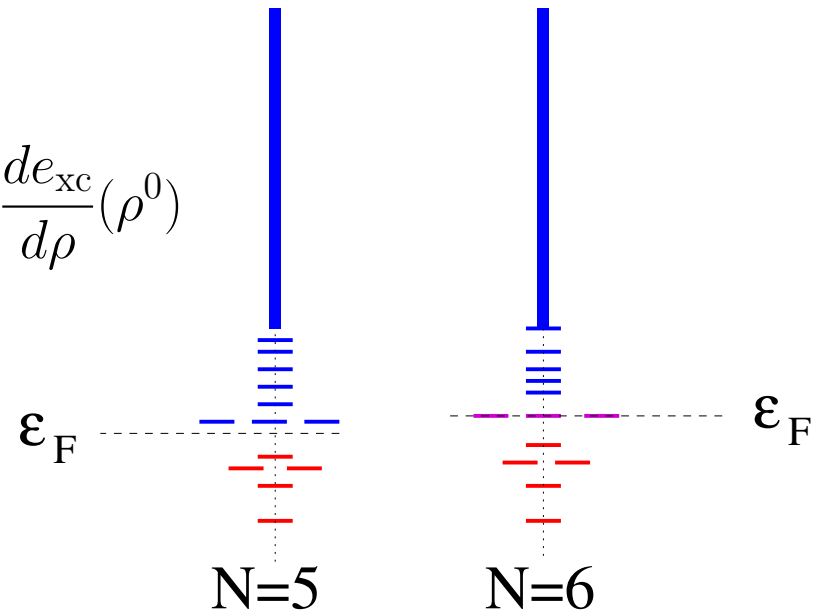
$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad 0 \leq n_i \leq 1, \quad \sum_{i=1}^{+\infty} n_i = N, \quad \phi_i \in H^1(\mathbb{R}^3).$$

Extended Kohn-Sham LDA equations

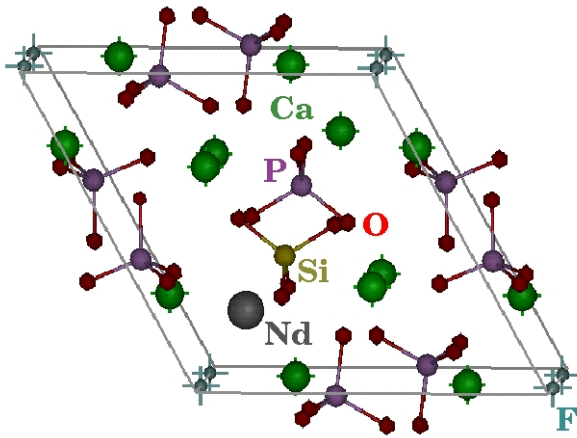
$$\gamma^0 = \sum_i n_i |\phi_i\rangle \langle \phi_i| \qquad \rho^0(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$$

$$\left\{ \begin{array}{l} H_{\rho^0} \phi_i = \varepsilon_i \phi_i \\ \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} n_i = 1 \text{ if } \varepsilon_i < \varepsilon_F, \\ 0 \leq n_i \leq 1 \text{ if } \varepsilon_i = \varepsilon_F, \\ n_i = 0 \text{ if } \varepsilon_i > \varepsilon_F, \end{array} \right. \quad \sum_i n_i = N$$

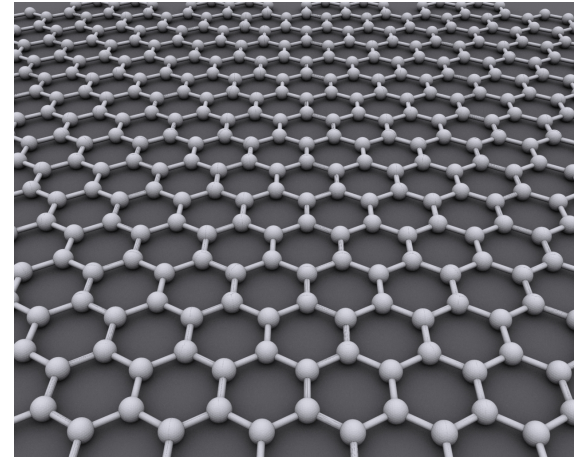
$$H_{\rho^0} = -\frac{1}{2}\Delta + V + \rho^0 \star |\mathbf{r}|^{-1} + \frac{de_{xc}}{d\rho}(\rho^0)$$



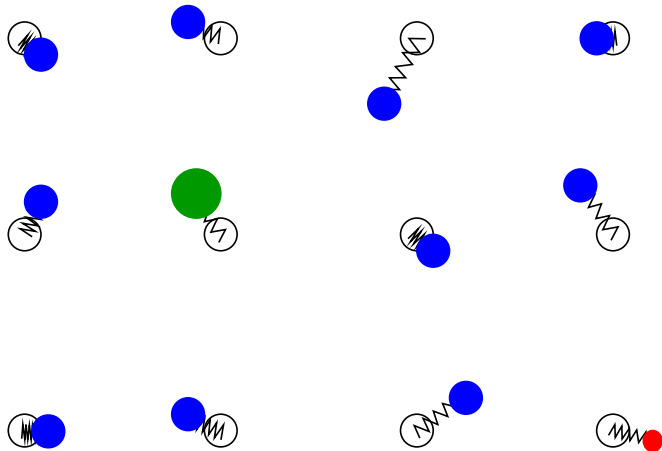
4 - Infinite systems



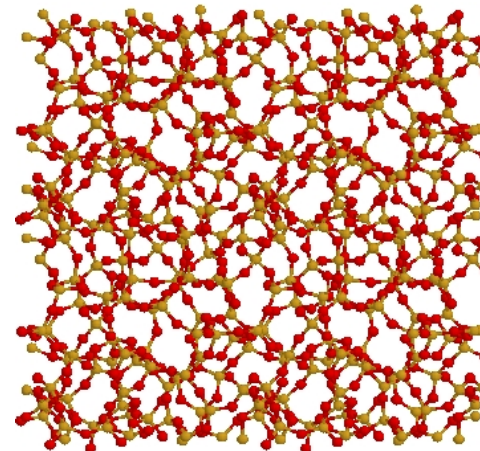
Periodic 3D system



Periodic 2D system

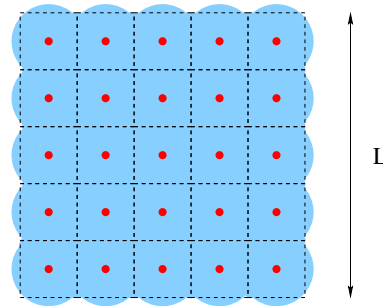


Alloy at finite temperature



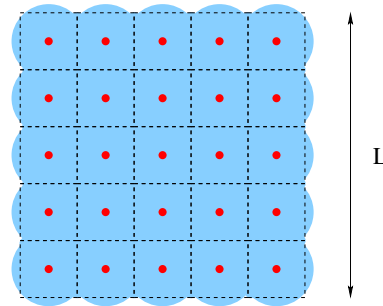
Amorphous system

Thermodynamic limit (bulk limit) for perfect crystals



$$\left\{ \begin{array}{l} \rho_L^{\text{nuc}} = \sum_{\mathbf{R} \in \mathbb{Z}^3 \cap (-L/2, L/2]^3} z m(\cdot - \mathbf{R}) \\ zL^3 \text{ electrons} \end{array} \right. \longrightarrow \left\{ \begin{array}{l} E_L^0 \quad \text{ground state total energy} \\ \rho_L^0 \quad \text{(unique) ground state density} \\ \gamma_L^0 \quad \text{a ground state density matrix} \end{array} \right.$$

Thermodynamic limit (bulk limit) for perfect crystals



$$\left\{ \begin{array}{l} \rho_L^{\text{nuc}} = \sum_{\mathbf{R} \in \mathbb{Z}^3 \cap (-L/2, L/2]^3} z m(\cdot - \mathbf{R}) \\ zL^3 \text{ electrons} \end{array} \right. \longrightarrow \left\{ \begin{array}{l} E_L^0 \text{ ground state total energy} \\ \rho_L^0 \text{ (unique) ground state density} \\ \gamma_L^0 \text{ a ground state density matrix} \end{array} \right.$$

Theorem (Catto-Le Bris-Lions, '01). For the Hartree model (KS with no xc)

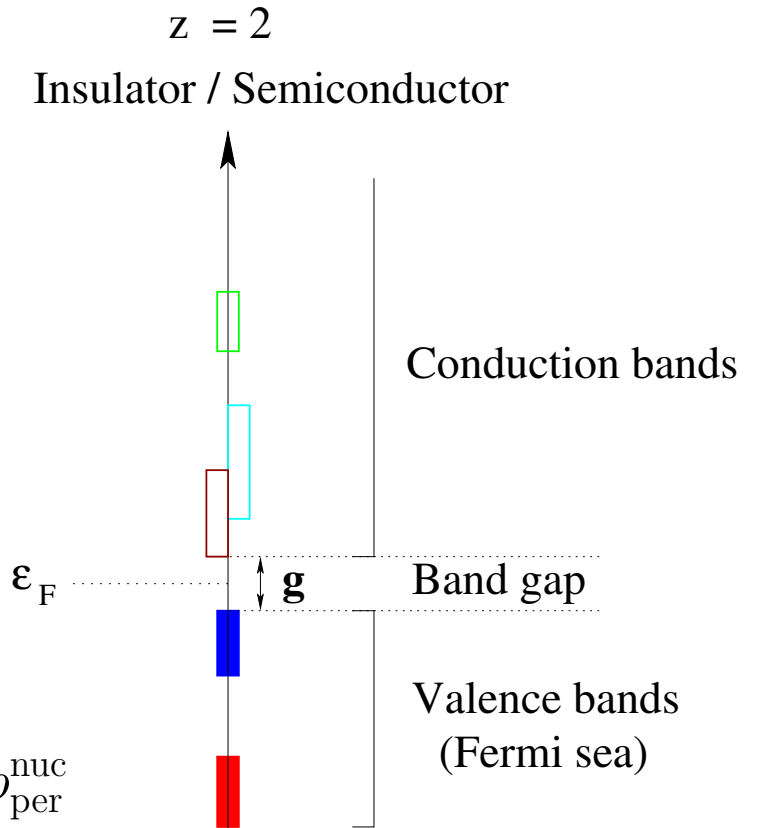
$$\lim_{L \rightarrow \infty} \frac{E_L^0}{L^3} = E_{\text{per}}^0, \quad \rho_L^0 \xrightarrow[L \rightarrow \infty]{\text{in some sense}} \rho_{\text{per}}^0, \quad \gamma_L^0 \xrightarrow[L \rightarrow \infty]{\text{in some sense}} \gamma_{\text{per}}^0.$$

Periodic Kohn-Sham equations

$$\left\{ \begin{array}{l}
 H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0 + V_{\text{per}}^{\text{xc}} \\
 -\Delta V_{\text{per}}^0 = 4\pi (\rho_{\text{per}}^{\text{nuc}} - \rho_{\text{per}}^0), \quad V_{\text{per}}^0 \text{ } \mathbb{Z}^3\text{-periodic} \\
 \rho_{\text{per}}^0(\mathbf{r}) \stackrel{\text{formally}}{=} \gamma_{\text{per}}^0(\mathbf{r}, \mathbf{r}) \\
 V_{\text{per}}^{\text{xc}}(\mathbf{r}) = \frac{de_{\text{xc}}}{d\rho}(\rho_{\text{per}}^0(\mathbf{r})) \quad \textbf{(LDA)} \\
 \gamma_{\text{per}}^0 = \mathbb{1}_{(-\infty, \varepsilon_{\text{F}})}(H_{\text{per}}^0), \quad \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^0 = \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^{\text{nuc}}
 \end{array} \right.$$

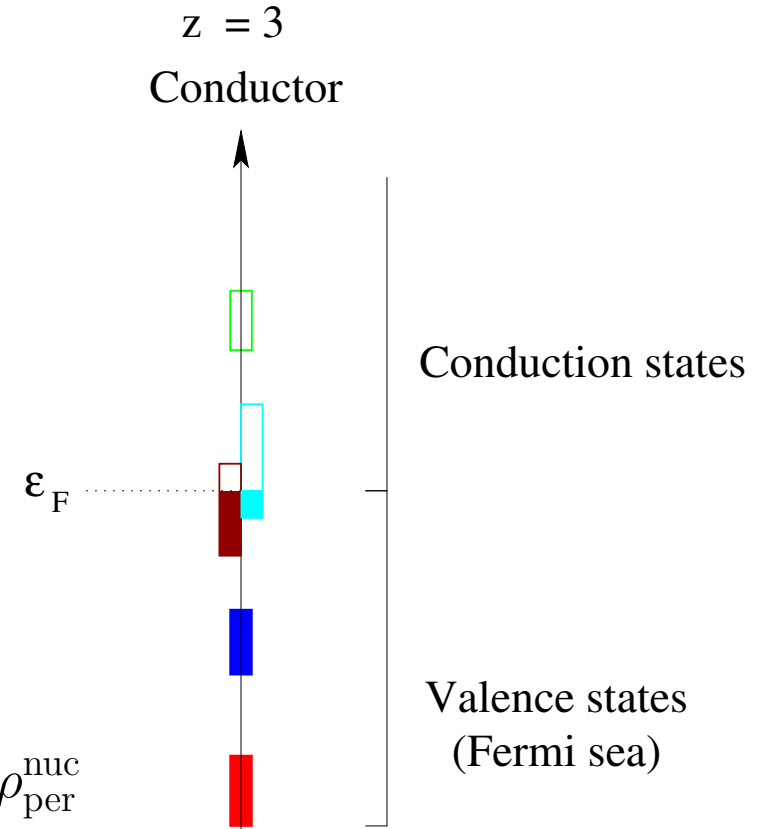
Periodic Kohn-Sham equations

$$\left\{ \begin{array}{l}
 H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0 + V_{\text{per}}^{\text{xc}} \\
 -\Delta V_{\text{per}}^0 = 4\pi (\rho_{\text{per}}^{\text{nuc}} - \rho_{\text{per}}^0), \quad V_{\text{per}}^0 \text{ } \mathbb{Z}^3\text{-periodic} \\
 \rho_{\text{per}}^0(\mathbf{r}) \stackrel{\text{formally}}{=} \gamma_{\text{per}}^0(\mathbf{r}, \mathbf{r}) \\
 V_{\text{per}}^{\text{xc}}(\mathbf{r}) = \frac{de_{\text{xc}}}{d\rho}(\rho_{\text{per}}^0(\mathbf{r})) \quad \text{(LDA)} \\
 \gamma_{\text{per}}^0 = \mathbb{1}_{(-\infty, \epsilon_F)}(H_{\text{per}}^0), \quad \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^0 = \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^{\text{nuc}}
 \end{array} \right.$$

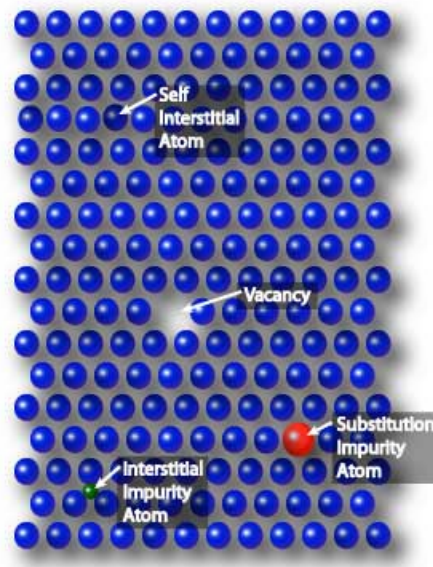


Periodic Kohn-Sham equations

$$\left\{ \begin{array}{l}
 H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0 + V_{\text{per}}^{\text{xc}} \\
 -\Delta V_{\text{per}}^0 = 4\pi (\rho_{\text{per}}^{\text{nuc}} - \rho_{\text{per}}^0), \quad V_{\text{per}}^0 \text{ } \mathbb{Z}^3\text{-periodic} \\
 \rho_{\text{per}}^0(\mathbf{r}) \stackrel{\text{formally}}{=} \gamma_{\text{per}}^0(\mathbf{r}, \mathbf{r}) \\
 V_{\text{per}}^{\text{xc}}(\mathbf{r}) = \frac{de_{\text{xc}}}{d\rho}(\rho_{\text{per}}^0(\mathbf{r})) \quad \text{(LDA)} \\
 \gamma_{\text{per}}^0 = \mathbb{1}_{(-\infty, \varepsilon_{\text{F}})}(H_{\text{per}}^0), \quad \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^0 = \int_{[-\frac{1}{2}, \frac{1}{2}]^3} \rho_{\text{per}}^{\text{nuc}}
 \end{array} \right.$$



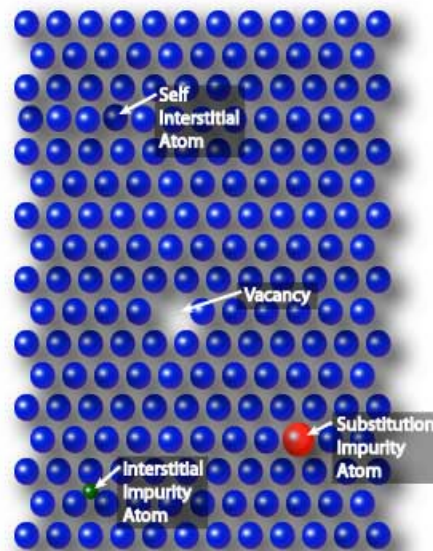
Thermodynamic limit for crystals with defects



*Crystals are like people,
it is their defects
that make them interesting*

(attributed to F. C. Franck)

Thermodynamic limit for crystals with defects



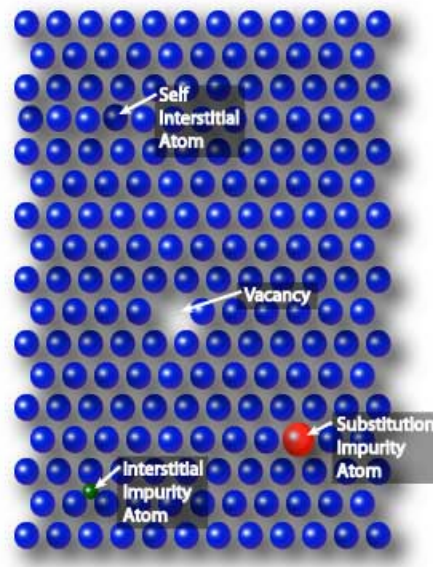
*Crystals are like people,
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DFT models for a single defect (or a finite number of defects)

- **TF:** Lieb-Simon ('77), TFW: Catto-Le Bris-Lions ('98)
- **Hartree:** EC, Deleurence, Lewin ('08), EC, Lewin ('10), Franck, Lewin, Lieb, Seiringer ('11), EC, Stoltz ('12), Gontier-Lahbabi ('16)
- **LDA:** EC, Deleurence, Lewin ('08)

Thermodynamic limit for crystals with defects



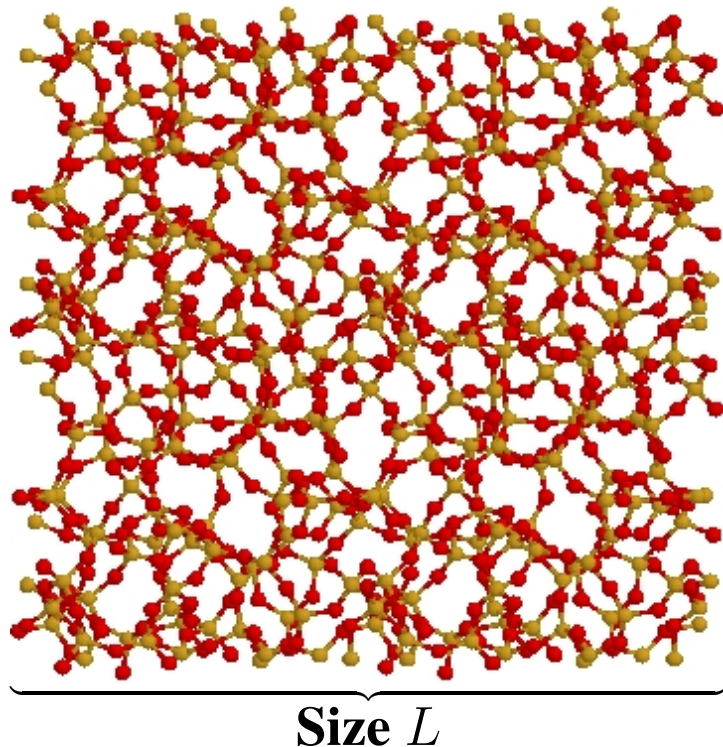
*Crystals are like people,
it is their defects
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(attributed to F. C. Franck)

DFT models for stationary random distributions of defects

- TFW: Blanc, Le Bris, Lions '07
- Hartree (**short-range interaction only**): EC, Lahbabi, Lewin, '13

Supercell method for Kohn-Sham simulations in the condensed phase



$$\left\{ \begin{array}{l} H_{L,\text{per}}^0 = -\frac{1}{2}\Delta + V_{L,\text{per}}^0 + V_{L,\text{per}}^{\text{xc}} \quad \text{on } L_{\text{per}}^2 \left(\left[-\frac{L}{2}, \frac{L}{2} \right]^3 \right) \\ -\Delta V_{L,\text{per}}^0 = 4\pi \left(\rho_{\text{per}}^{L,\text{nuc}} - \rho_{L,\text{per}}^0 \right), \quad V_{L,\text{per}}^0 \text{ } L\mathbb{Z}^3\text{-periodic} \\ \rho_{L,\text{per}}^0(\mathbf{r}) \stackrel{\text{formally}}{=} \gamma_{L,\text{per}}^0(\mathbf{r}, \mathbf{r}) \\ \gamma_{L,\text{per}}^0 = \mathbb{1}_{(-\infty, \varepsilon_{\text{F}})}(H_{L,\text{per}}^0), \quad \int_{\left[-\frac{L}{2}, \frac{L}{2} \right]^3} \rho_{L,\text{per}}^0 = \int_{\left[-\frac{L}{2}, \frac{L}{2} \right]^3} \rho_{\text{per}}^{\text{nuc}} \end{array} \right.$$

For infinite, macroscopically homogeneous, systems:

supercell method \sim representative volume method (RVP) of stochastic homogenization

Converges when $L \rightarrow \infty$ for the Hartree model for perfect crystals (\Leftrightarrow uniform Brillouin zone discretization) and crystals with a single defect.

5 - Standard discretization methods and algorithms

Quantum chemistry	Solid state physics/materials science
Finite systems	Infinite systems (supercell method)
Gaussian atomic orbitals	Planewaves
Some popular AO codes: Gaussian, Molpro, Q-Chem	Some popular PW codes: Abinit, CASTEP, Quantum Espresso, VASP

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

Galerkin approximation of the Kohn-Sham LDA model (finite systems)

$$E_0 \simeq \inf \left\{ E^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$E^{\text{KS}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} \rho_{\Phi} V + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi}(\mathbf{r}) \rho_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int_{\mathbb{R}^3} e_{\text{xc}}^{\text{LDA}}(\rho_{\Phi}(\mathbf{r})) d\mathbf{r}$$

with
$$V(\mathbf{r}) = - \sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|} \quad \rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2.$$

Approximation space: $\mathcal{X} = \text{Span}(\chi_1, \dots, \chi_{N_b}) \subset H^1(\mathbb{R}^3)$, $\text{dim}(\mathcal{X}) = N_b$.

$$E_0^{\text{KS}} \leq E_{0,\mathcal{X}}^{\text{KS}} = \inf \left\{ E^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}^N, \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \right\}$$

$$\Phi = (\phi_1, \dots, \phi_N) \in \mathcal{X}^N \quad \Rightarrow \quad \phi_i(\mathbf{r}) = \sum_{\mu=1}^{N_b} C_{\mu i} \chi_{\mu}(\mathbf{r})$$

Discretized formulation of the Kohn-Sham model

$$E_{0,\mathcal{X}}^{\text{KS}} = \inf \{ E^{\text{KS}}(CC^T), C \in \mathbb{R}^{N_b \times N}, C^T SC = I_N \}$$

$$E^{\text{KS}}(D) = \mathbf{Tr}(hD) + \frac{1}{2} \mathbf{Tr}(J(D)D) + E_{\text{xc}}^{\text{LDA}}(D), \quad [J(D)]_{\mu\nu} = \sum_{\kappa\lambda} (\mu\nu|\kappa\lambda) D_{\kappa\lambda}$$

Electronic integrals

- **Overlap matrix:** $S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu$
- **Core Hamiltonian matrix:** $h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu - \sum_{k=1}^M z_k \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r}$
- **Two-electron integrals:** $(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\kappa(\mathbf{r}') \chi_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

Fundamental remark (Boys 1950): if the χ_μ are **gaussian-polynomials**

$$\chi_\mu(\mathbf{r}) = p(\mathbf{r}) \exp(-\alpha|\mathbf{r}|^2)$$

then the one-electron integrals

$$S_{\mu\nu} = \int_{\mathbb{R}^3} \chi_\mu \chi_\nu, \quad h_{\mu\nu} = \frac{1}{2} \int_{\mathbb{R}^3} \nabla \chi_\mu \cdot \nabla \chi_\nu + \int_{\mathbb{R}^3} V^{\text{ne}} \chi_\mu \chi_\nu$$

and the two-electron integrals

$$(\mu\nu|\kappa\lambda) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\kappa(\mathbf{r}') \chi_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

can be computed analytically.

The exchange-correlation energy is computed by numerical quadrature with a partition of identity:

$$E_{\text{xc}}^{\text{LDA}}(D) \simeq \sum_{k=1}^M \left(\sum_{g=1}^{N_k} w_{k,g}(\{\mathbf{R}_j\}) e_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{R}_k + \mathbf{r}_{k,g})) \right) \quad \text{with} \quad \rho(\mathbf{r}) = \sum_{\mu,\nu=1}^{N_b} D_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})$$

Atomic orbital basis sets

1. A collection $\{\xi_{\mu}^A\}_{1 \leq \mu \leq n_A}$ of n_A linearly independent linear combination of gaussian polynomials are associated with each chemical element A of the periodic table: these are the atomic orbitals of A .
2. To perform a calculation on a given chemical system, one builds a basis $\{\chi_{\mu}\}$ by putting together all the atomic orbitals related to all the atoms of the system.

Example of the water molecule H_2O

$$\{\chi_{\mu}\} = \left\{ \xi_1^H(\mathbf{r} - \mathbf{R}_{H_1}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_1}); \xi_1^H(\mathbf{r} - \mathbf{R}_{H_2}), \dots, \xi_{n_H}^H(\mathbf{r} - \mathbf{R}_{H_2}); \xi_1^O(\mathbf{r} - \mathbf{R}_O), \dots, \xi_{n_O}^O(\mathbf{r} - \mathbf{R}_O) \right\},$$

where \mathbf{R}_{H_1} , \mathbf{R}_{H_2} and \mathbf{R}_O denote the positions in \mathbb{R}^3 of the Hydrogen nuclei and of the Oxygen nucleus respectively.

Typically: $N_b \sim 2N$ (small atomic basis set) to $10N$ (large atomic basis set).

Molecular orbital formulation

For simplicity, the basis $\{\chi_\mu\}_{1 \leq \mu \leq N_b}$ is assumed to be orthonormal.

$$E_{0,\mathcal{X}}^{\text{KS}} = \inf \{ E^{\text{KS}}(CC^T), C \in \mathcal{C} \}$$

$$\mathcal{C} = \{ C \in \mathbb{R}^{N_b \times N}, C^T C = I_N \} \quad \text{(Stiefel manifold)}$$

$$E^{\text{KS}}(D) = \mathbf{Tr}(hD) + \frac{1}{2} \mathbf{Tr}(J(D)D) + E_{\text{xc}}^{\text{LDA}}(D)$$

↑
linear

↑
quadratic

↑
"small" term

Density matrix formulation

When C varies in the set $\mathcal{C} = \{C \in \mathbb{R}^{N_b \times N}, C^T C = I_N\}$, $D = CC^T$ spans

$$\mathcal{P} = \{D \in \mathbb{R}^{N_b \times N_b}, D = D^T, \mathbf{Tr}(D) = N, D^2 = D\}$$

$$= \{ \text{rank-}N \text{ orthogonal projectors of } \mathbb{R}^{N_b \times N_b} \} \quad \text{(Grassmann manifold)}$$

Therefore,

$$E_{0,\mathcal{X}}^{\text{KS}} = \inf \{ E^{\text{KS}}(D), D \in \mathcal{P} \},$$

$$E^{\text{KS}}(D) = \mathbf{Tr}(hD) + \frac{1}{2} \mathbf{Tr}(J(D)D) + E_{\text{xc}}^{\text{LDA}}(D)$$

↑
linear

↑
quadratic

↑
"small" term

Discretized Kohn-Sham equations (general case of a non-orthogonal basis)

$$\left\{ \begin{array}{l} D = CC^T, \quad F = h + J(D) + F_{xc}^{LDA}(D) \\ F\Phi_i = \varepsilon_i S\Phi_i, \quad \varepsilon_1 \leq \dots \leq \varepsilon_N \text{ lowest gen. eig. of } F\Phi = \varepsilon S\Phi, \quad \Phi_i^T S\Phi_j = \delta_{ij} \\ C = (\Phi_1, \dots, \Phi_N) \end{array} \right.$$

$$D \in \mathbb{R}_{\text{sym}}^{N_b \times N_b}, \quad F \in \mathbb{R}_{\text{sym}}^{N_b \times N_b}, \quad \Phi_i \in \mathbb{R}^{N_b}, \quad C \in \mathbb{R}^{N_b \times N}$$

Solutions to the discretized Kohn-Sham problem can be obtained

- either by solving a constrained optimization problem (on a Stiefel or a Grassmann manifold);
- or by solving the above equations by means of a self-consistent field (SCF) algorithm.

The design of more efficient methods, in particular for very large molecular systems, is still an active field of research.

Kohn-Sham LDA model with periodic boundary conditions (supercell method)

Ω : supercell, \mathcal{R} : direct lattice, \mathcal{R}^* : dual lattice, $e_{\mathbf{K}}(\mathbf{r}) = |\Omega|^{-1/2} e^{i\mathbf{K}\cdot\mathbf{r}}$

$$E_0^{\text{KS}} = \inf \left\{ E^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (H_{\#}^1(\Omega))^N, \int_{\Omega} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} \right\}$$

$$E^{\text{KS}}(\Phi) = \frac{1}{2} \sum_{i=1}^N \int_{\Omega} |\nabla \phi_i|^2 + \int_{\Omega} \rho_{\Phi} V_{\text{local}} + \sum_{i=1}^N \langle \phi_i | V_{\text{nl}} | \phi_i \rangle + J(\rho_{\Phi}) + E_{\text{xc}}^{\text{LDA}}(\rho_{\Phi})$$

$$H_{\#}^1(\Omega) = \{ \phi \in H_{\text{loc}}^1(\mathbb{R}^3) \mid \phi \text{ } \mathcal{R}\text{-periodic} \}$$

$$\rho_{\Phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad J(\rho) = 2\pi \sum_{\mathbf{K} \in \mathcal{R}^* \setminus \{0\}} \frac{|\widehat{\rho}_{\mathbf{K}}|^2}{|\mathbf{K}|^2} \quad E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\Omega} e_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r})) d\mathbf{r}$$

All electron calculations: $N, Z =$ number of electrons / protons in Ω ,

$$V_{\text{nl}} = 0, \quad V_{\text{local}} : \mathcal{R}\text{-periodic solution to } -\Delta V_{\text{local}} = 4\pi (\rho_{\text{nuc}}^{\text{per}} - Z).$$

Pseudopotential calculation: $N =$ number of valence electrons in Ω ,

V_{local} and V_{nl} : local and nonlocal parts of the pseudopotential.

Planewave discretization of Kohn-Sham models with pseudopotentials

$$E_0^{\text{KS}} \leq E_0^{\text{KS}, E_c} := \inf \left\{ E^{\text{KS}}(\Phi), \Phi = (\phi_1, \dots, \phi_N) \in (X_{E_c})^N, \int_{\Omega} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij} \right\}$$

$$X_{E_c} = \left\{ \phi(\mathbf{r}) = \sum_{\mathbf{K} \in \mathcal{R}^*, |\mathbf{K}|^2/2 \leq E_c} \phi_{\mathbf{K}} e_{\mathbf{K}}(\mathbf{r}), \phi_{-\mathbf{K}} = \overline{\phi_{\mathbf{K}}} \right\}, \quad e_{\mathbf{K}}(\mathbf{r}) = |\Omega|^{-1/2} e^{i\mathbf{K} \cdot \mathbf{r}}.$$

Typically: $N_b \sim \frac{\sqrt{2}}{6\pi^2} |\Omega| E_c^{3/2} \sim 100N$ to $1000N$ for usual systems/pseudopotentials.

Various strategies can be used to solve the above constrained optimization problem or the associated Euler-Lagrange equations. They all are iterative methods based on computations of matrix-vector products $\widehat{\mathbb{H}}\widehat{\mathbb{X}}$, where

- $\widehat{\mathbb{H}}$ is the matrix of some periodic Schrödinger operator $H = -\frac{1}{2}\Delta + V_{\text{per}}$ in the Fourier basis $(e_{\mathbf{K}})$ of X_{E_c} ;
- $\widehat{\mathbb{X}}$ is a vector containing the Fourier coefficients of some orbital $\phi \in X_{E_c}$.

Such matrix-vector products can be computed in $O(N_b \log N_b)$ operations by means of Fast Fourier Transform (FFT).

6 - Advanced methods and current research

Improvements of available DFT models

- Construction of better exchange-correlation functionals
- Multi-reference DFT
- DFT+U
- ...

Many prominent physicists and chemists are working on these issues (Becke, Burke, Langreth, Perdew, Savin, Scuseria, Scheffler, Tkatchenko, Truhlar, Yang, ... among many others).

Very few mathematical works:

Cotar, Friesecke and Klüppelberg, *Density Functional Theory and optimal transportation with Coulomb cost*, CPAM '13.

Chen and Friesecke, *Pair densities in density functional theory*, MMS '15.

Advanced numerical algorithms for Kohn-Sham : many works published in both the physics/chemistry and the applied mathematics literatures.

Example: alternatives to diagonalization for localized orbital methods

Given a real symmetric matrix $H \in \mathbb{R}^{n \times n}$ and $\mu \in \mathbb{R}$, compute the density matrix $D = \mathbb{1}_{(-\infty, \mu]}(H)$.

Naive way to proceed

1. Diagonalize the matrix H in an orthonormal basis

$$H\Phi_i = \varepsilon_i\Phi_i, \quad \Phi_i \in \mathbb{R}^n, \quad \Phi_j^T\Phi_i = \delta_{ij}, \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_n$$

2. Compute the density matrix using the formula

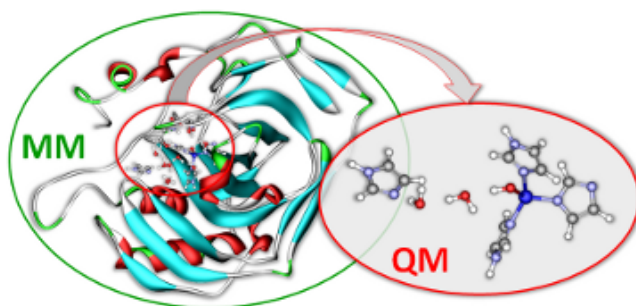
$$D = \mathbb{1}_{(-\infty, \mu]}(H) = \sum_{i | \varepsilon_i \leq \mu} \Phi_i\Phi_i^T.$$

One possible alternative: make use of the Cauchy formula

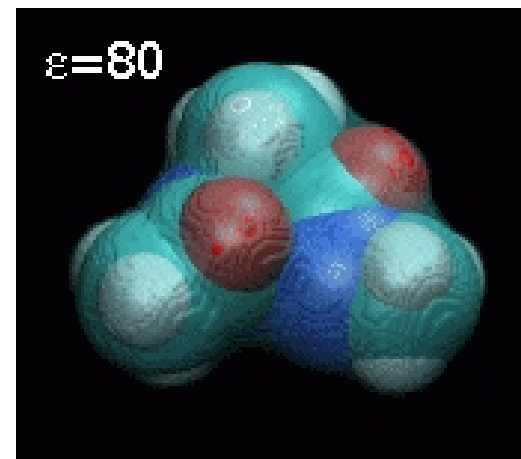
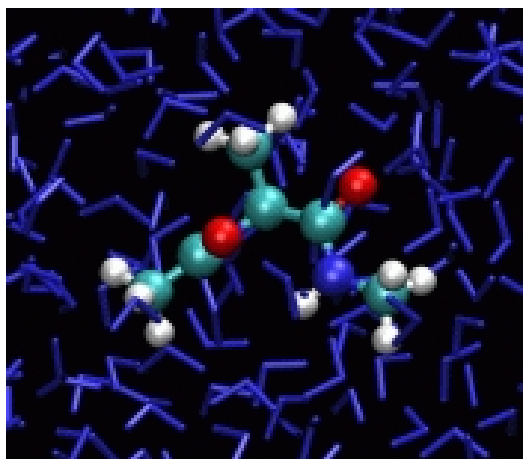
$$D = \frac{1}{2i\pi} \oint_{\mathcal{C}} (z - H)^{-1} dz.$$

Multiscale models for large systems (2013 Nobel prize in Chemistry)

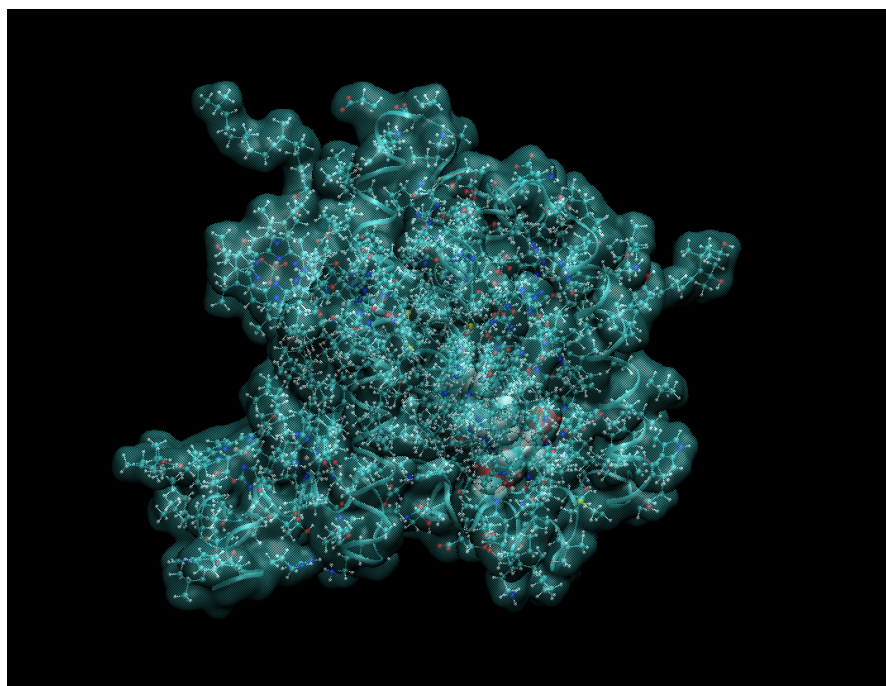
- QM/MM (quantum mechanics/molecular mechanics)



- QM/PCM (quantum mechanics/polarizable continuum models)



Improvement of numerical algorithms for QM/MM/PCM models: series of work by EC, Lipparini, Mennucci, Maday, Stamm, et al '13-'16

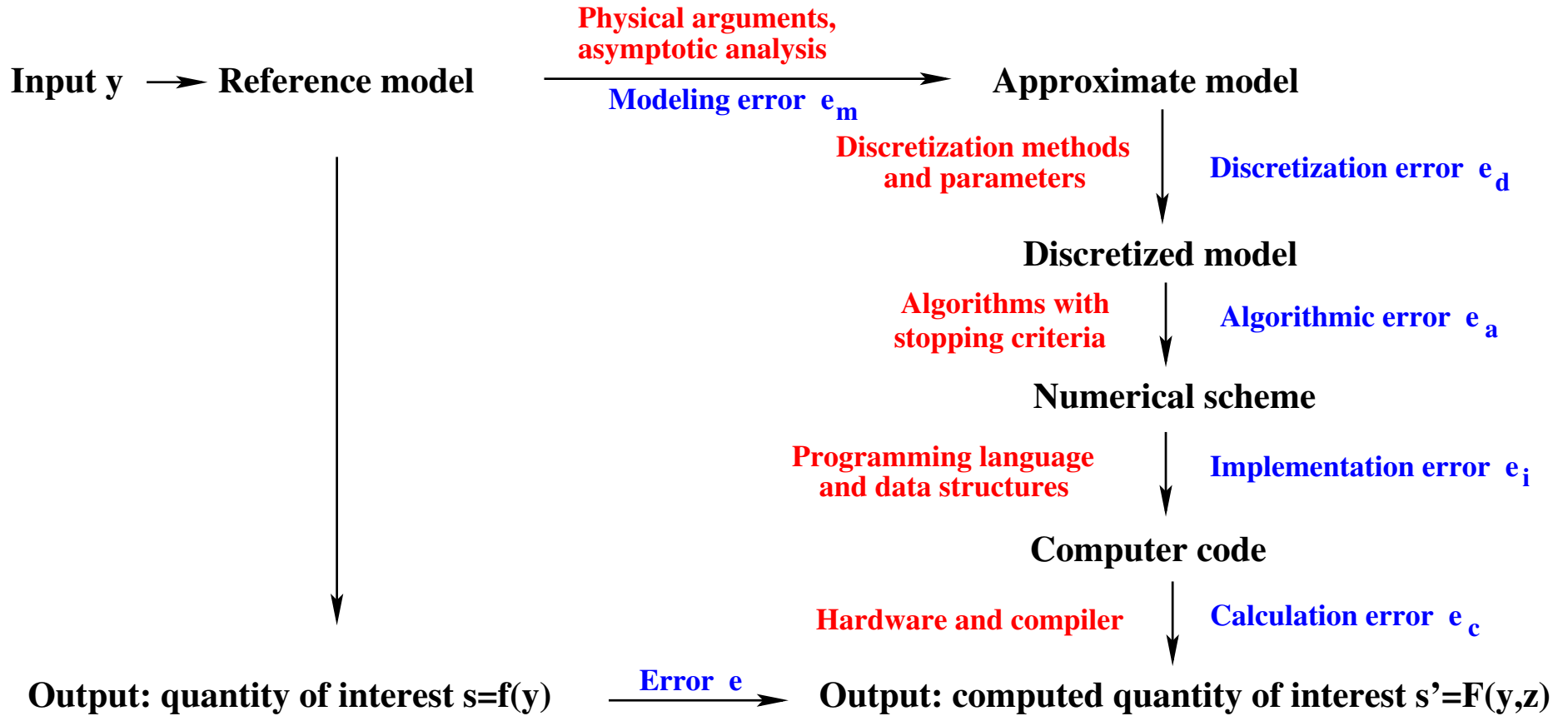


QM/MM/PCM simulation (Mennucci et al.)

A comprehensive analysis of why (or when) QM/MM work is still missing

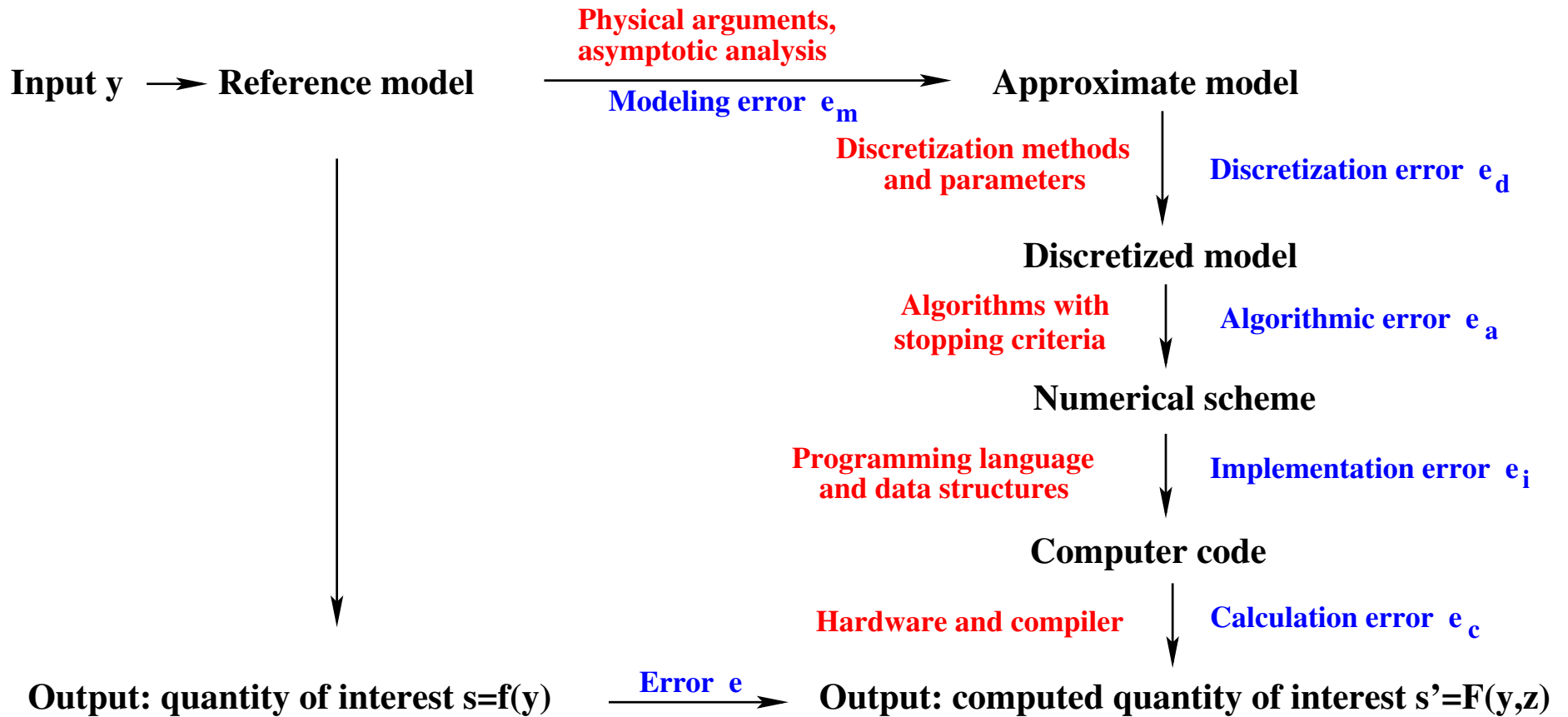
H. Chen and C. Ortner. *QM/MM methods for crystalline defects*. Part I: MMS '16, Part II: MMS '17.

Error estimators



Total error: $e = e_m + e_d + e_a + e_i + e_c$

Error estimators

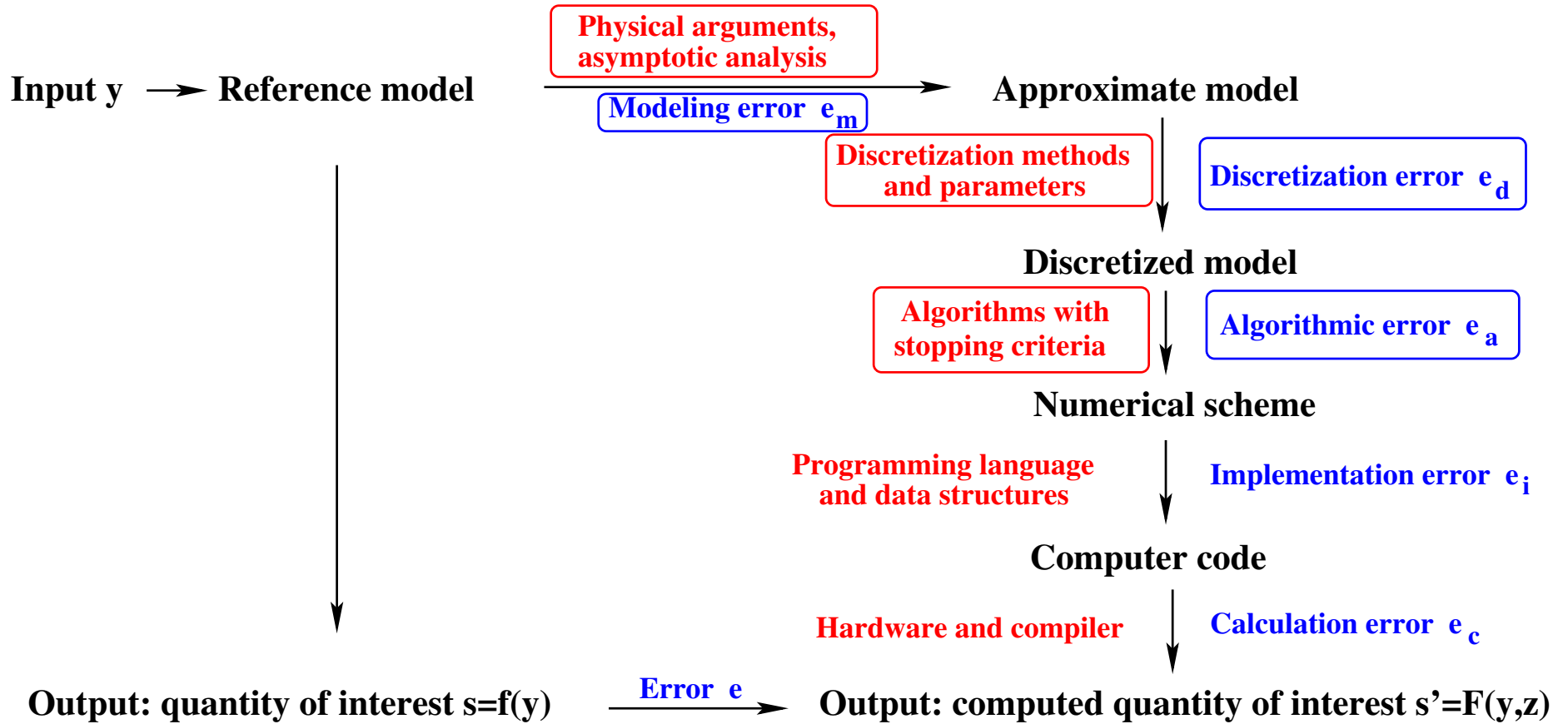


Total error: $e = e_m + e_d + e_a + e_i + e_c$

Goal 1: provide error estimates (certification)

Goal 2: minimize the computation cost to obtain the desired accuracy.

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- **Human error (bugs): manual/automatic code validation.**

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 - **Between Jan. 1982 and Nov. 1983, Vancouver stock exchange dropped from 1,000 to 524 instead of going up to 1,098 due to truncation errors.**
 - **Patriot missile failure (Feb. 1991) due to round-off errors: storage of 0.1 on 24 bits only in the internal clock (500 m drift after 100 h).**
 - **Ariane 5 rocket crash (Jun. 1996) due to overflow errors during the conversion of 64-bit floating point numbers into 16-bit signed integers.**

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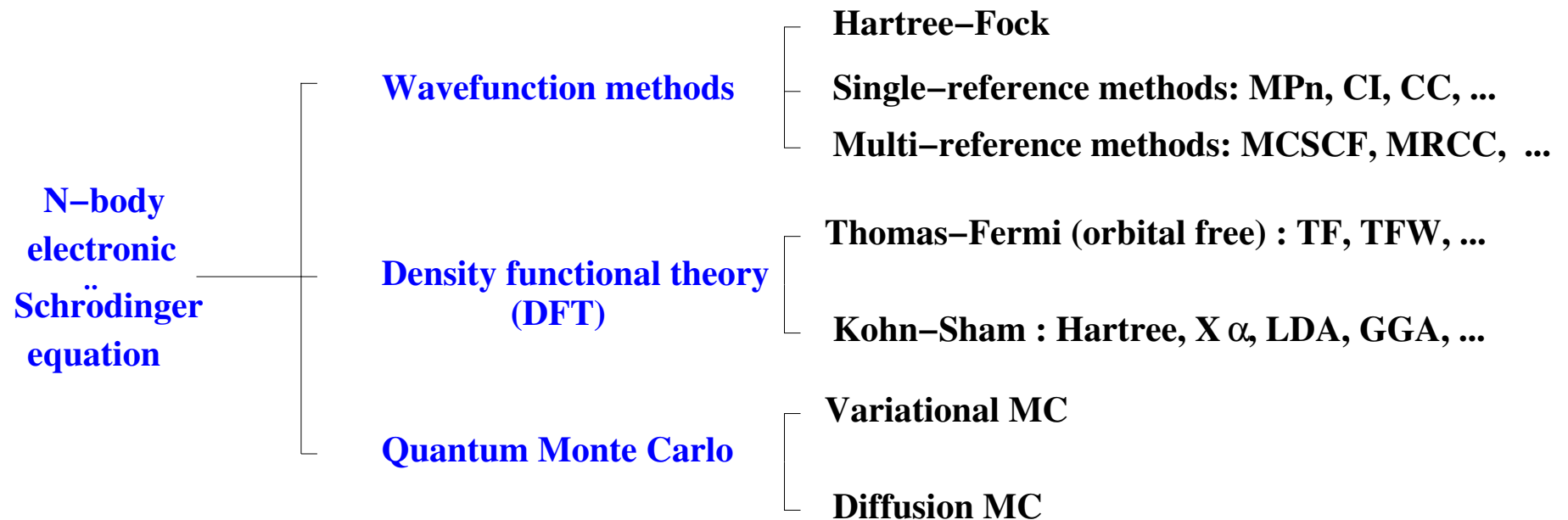
Computing error e_c

Resiliency will be one of the toughest challenges in future exascale systems. Memory errors contribute more than 40% of the total hardware-related failures and are projected to increase in future exascale systems. The use of error correction codes (ECC) and checkpointing are two effective approaches to fault tolerance. (Li et al. 2011)

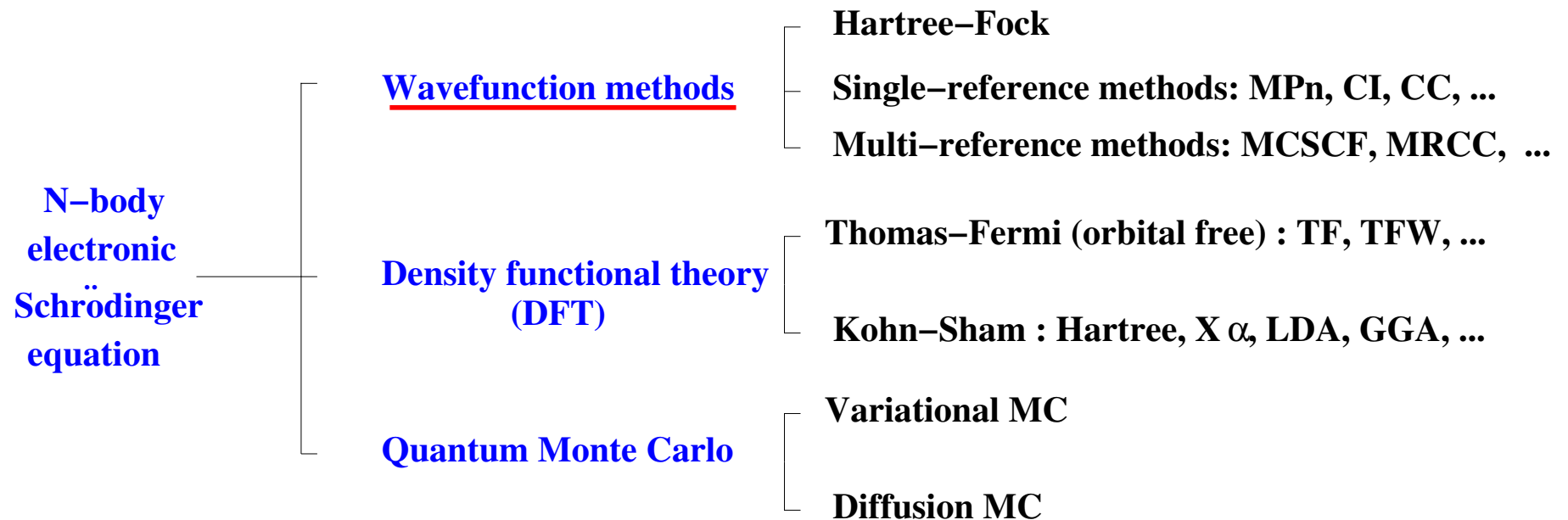
Discretization and algorithmic errors for periodic KS models

- **Optimal *a priori* error estimators for Kohn-Sham are available (EC, Chakir, Maday M2AN '12)**
- **Numerical quadrature errors can be estimated (EC, Chakir, Maday 'J. Sci. Comput. 10)**
- ***A posteriori* error estimators and computational load reduction strategies are under development: Lin, Yang et al. (Berkeley), Schneider et al. (Berlin), Zhou et al. (Beijing), our (Paris/Aahren) team (EC, Dusson, Maday, Stamm, Vohralík, J. Comp. Phys. '16)**
- **k-point sampling on the Brillouin zone for metals (EC, Ehrlacher, Gontier, Levitt, Lombardi, in prep.)**
- **Construction of optimized pseudopotentials (EC, Mourad CMS '16, Blanc, EC, Dupuy, in prep.)**
- **Error estimators on energy differences (EC, Dusson, arXiv:1701.04643).**

Model error e_m : can certified *a posteriori* error estimators be computed?

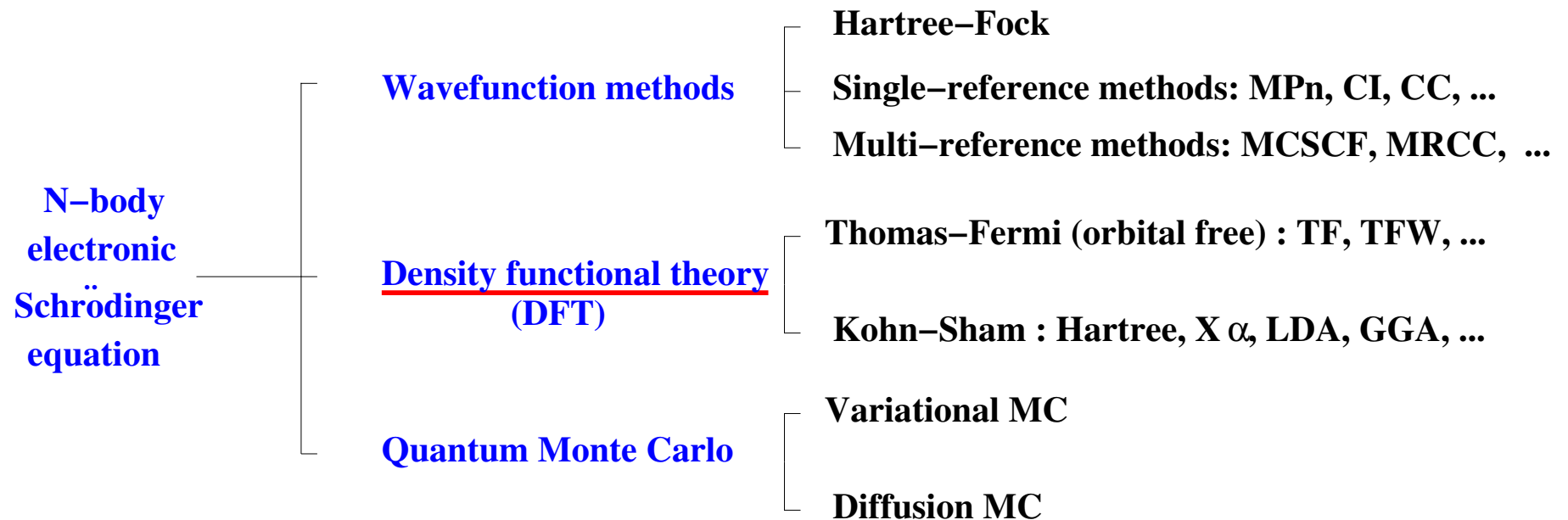


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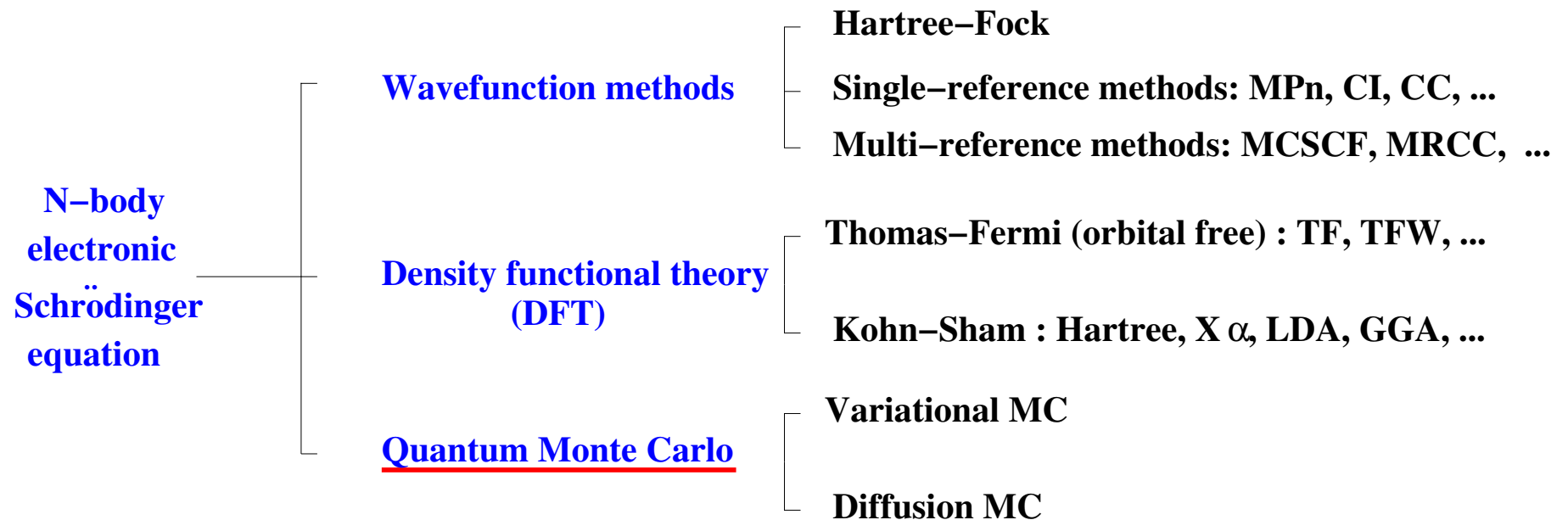
- **Wavefunction methods: yes, at least in principle**

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Model error e_m : can certified *a posteriori* error estimators be computed?



- **Wavefunction methods: yes, at least in principle**
- **Density functional theory: probably not**
- **Quantum Monte Carlo methods: maybe**

Educated choice of the exchange-correlation potential in DFT

$$\left\{ \begin{array}{l}
 \text{ground state density } \rho_0^{\{\mathbf{R}_k\}}(\mathbf{r}) = \rho_0(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \\
 \\
 -\frac{1}{2}\Delta\phi_i + V_{\rho_0}^{\text{KS}}\phi_i = \lambda_i\phi_i, \quad \lambda_1 < \lambda_2 \leq \lambda_3 \leq \dots \\
 \\
 \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \\
 \\
 V_{\rho_0}^{\text{KS}} = V_{\rho_0}^{\text{H}} + v_{\rho_0}^{\text{xc}} \quad v_{\rho_0}^{\text{xc}} : \text{ exchange-correlation potential} \\
 \\
 -\Delta V_{\rho_0}^{\text{H}} = 4\pi \left(\rho_0 - \sum_{k=1}^M z_k \delta_{\mathbf{R}_k} \right)
 \end{array} \right.$$

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Kieron Burke

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Kieron Burke

citations of the B3LYP paper (Google Scholar, May. 2016): 64,674

Educated choice of the exchange-correlation potential in DFT

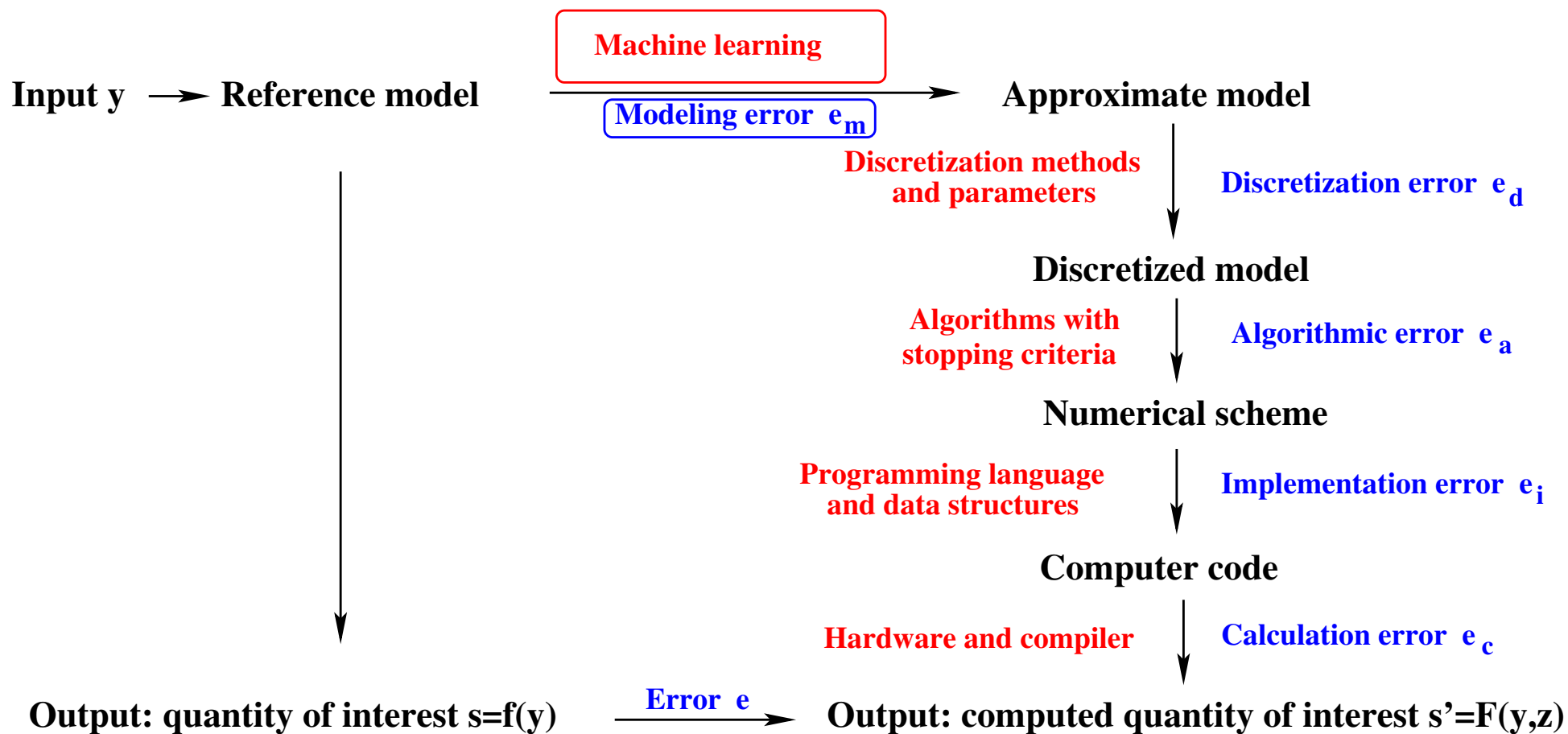
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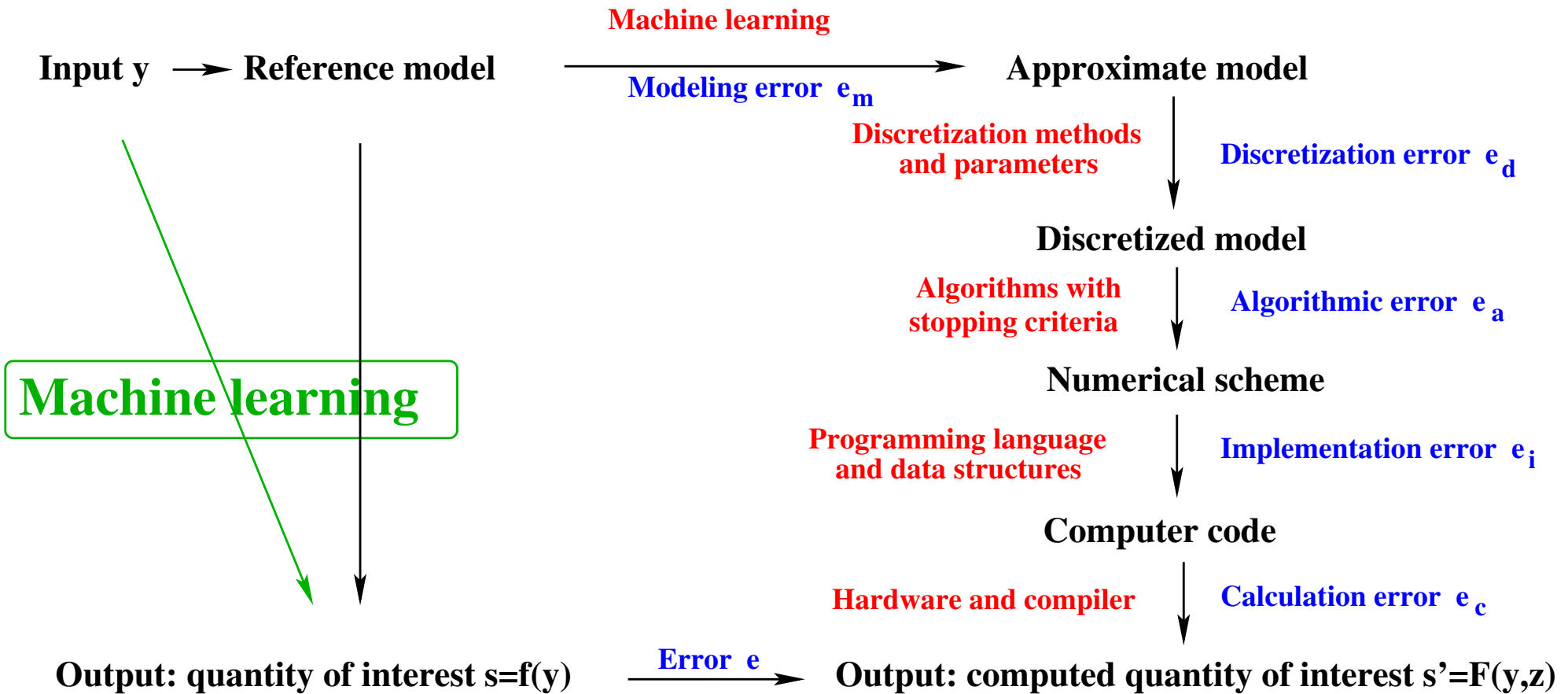
Kieron Burke

Can machine learning help?

Machine learning in molecular simulation: model selection



Machine learning in molecular simulation: direct computation of QOI



DFT calculations are used to compute the QOI in training and validation sets (Ceder et al '10, Rupp, Tkatchenko, Müller, von Lilienfeld '12, Burke et al. '12, Csányi et al. '13, Mallat et al. '14, ..., IPAM program '16)