Mathematical representations of quantum states

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IPAM, Los Angeles, Septembre 13-16, 2016

Outline of the tutorial

1. Quantum states of many-particle systems
2. First-principle molecular simulation (mathematical viewpoint)
3. Representations of electronic states

1 - Quantum states of many-particle systems

pure states vs mixed states

time-dependent states vs steady (or stationary) states

separable states vs entangled states

bound states vs scattering states

ground states vs excited states

First principles of 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 one to connect theory and exper.**

The system is said to be in a pure state at time t if its state can be 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 $\Psi(t) = f(t)\psi$, $f(t) \in \mathbb{C}$, $\psi \in \mathcal{H}$

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

Quantum mechanics for one-particle systems

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

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

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

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

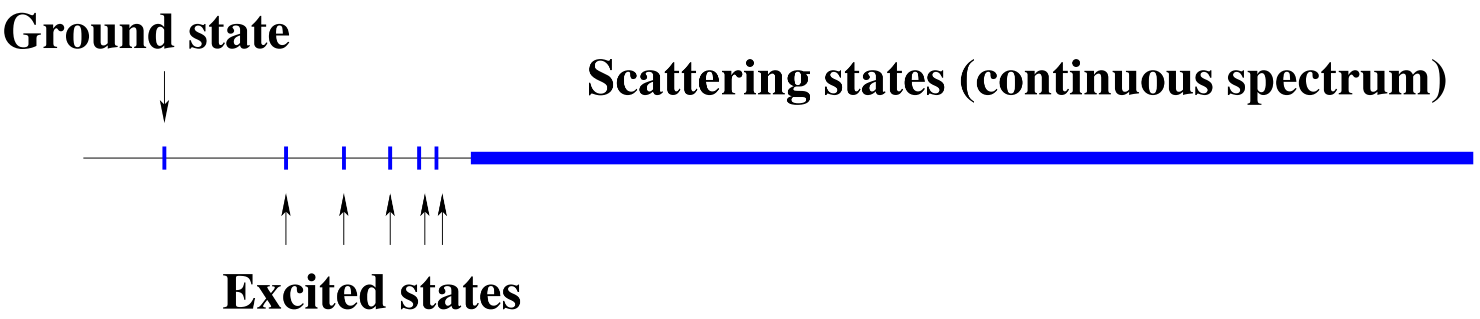
Time-dependent Schrödinger equation

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

Time-independent Schrödinger equation

$$\begin{cases} H\psi = E\psi \\ \|\psi\| = 1 \end{cases} \longrightarrow \begin{cases} -\dfrac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \\ \displaystyle\int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2 \, d\mathbf{r} = 1 \end{cases}$$

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


Ground state

Scattering states (continuous spectrum)

Excited states

Ex.: $V_{\text{ext}}(\mathbf{r}) = -\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}|}$ **(Hydrogen atom),** $\sigma(H) = \left\{-\dfrac{E_{\text{Ryd}}}{n^2}\right\}_{n\in\mathbb{N}^*} \cup [0, +\infty[$**.**

Physical meaning of the discrete energy levels

Example of the hydrogen atom

$$-\frac{\hbar^2}{2m_e}\Delta\Psi(x) - \frac{e^2}{4\pi\varepsilon_0|x|}\Psi(x) = E\Psi(x)$$

$$E_n = -\frac{E_{\mathrm{Ryd}}}{n^2}, \quad n \in \mathbb{N}^*, \quad E_{\mathrm{Ryd}} = \frac{m_e}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2, \quad \lambda_{m\to n} = \frac{8\pi\hbar c}{E_{\mathrm{Ryd}}}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)^{-1}$$

Balmer series (nm): $\lambda^{\mathrm{exp}}_{6\to2} = 410.17$, $\lambda^{\mathrm{exp}}_{5\to2} = 434.05$, $\lambda^{\mathrm{exp}}_{4\to2} = 486.13$, $\lambda^{\mathrm{exp}}_{3\to2} = 656.28$
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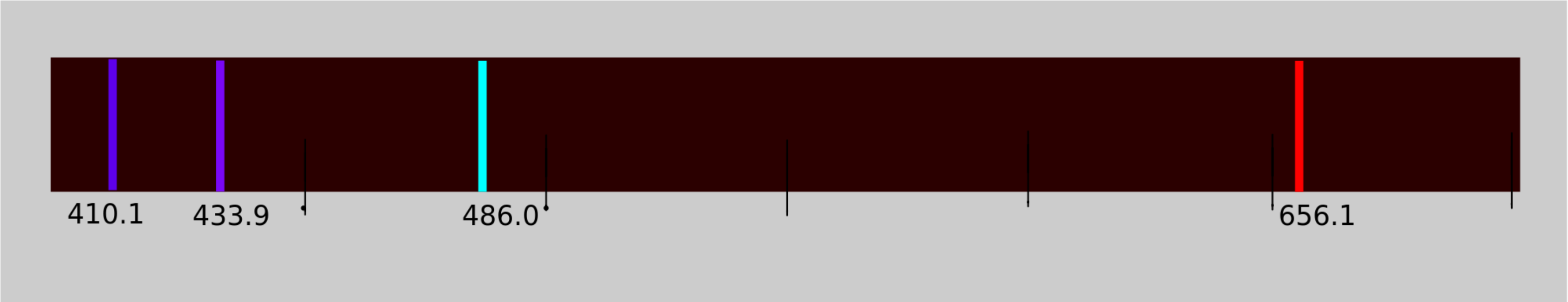

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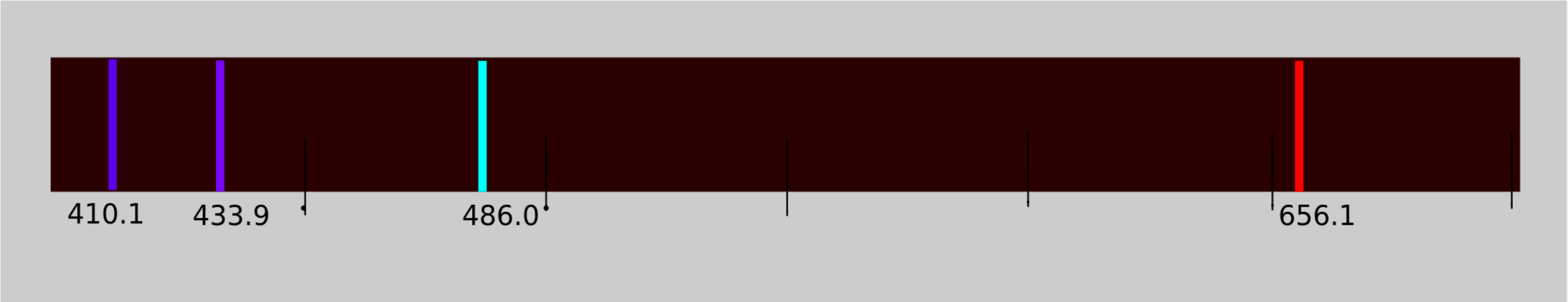

On the physical meaning of point and continuous spectra

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 $\mathcal{H}_p = \overline{\text{Span}\left\{\text{eigenvectors of } H\right\}}$ 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 $B_R = \left\{\mathbf{r} \in \mathbb{R}^d \mid |\mathbf{r}| < R\right\}$.

Then

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

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

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$\mathcal{H}_\mathrm{p} \sim$ set of bound states, $\mathcal{H}_\mathrm{c} \sim$ set of scattering states.

Important remarks

1. Quantum mechanics is an intrinsically probabilistic theory: according to the Copenhagen interpretation, the fact that two different experiments made on two identical systems in the same pure state do not necessarily lead to the same result is not due to an incomplete knowledge of the state.

   Historical milestones:

   - Einstein-Podolski-Rosen paradox ('35);
   - Bell inequalities ('64);
   - Aspect's experiments ('81).

2. The set of pure states of an isolated quantum system with state space $\mathcal{H}$ is diffeomorphic to the projective space $P(\mathcal{H}) \sim (\mathcal{H} \setminus \{0\})/\mathbb{C}^*$. This is the reason why the two wavefunctions ψ and $e^{i\alpha}\psi$, with $\psi \in \mathcal{H}$, $\|\psi\| = 1$ and $\alpha \in \mathbb{R}$, represent exactly the same state.

Composite quantum systems

If a system can be decomposed into two *distinguishable* quantum subsystems A and B, then the state space of this system is

$$\mathcal{H}_{AB} = \mathcal{H}_A \otimes \mathcal{H}_B,$$

where $\mathcal{H}_A$ and $\mathcal{H}_B$ are the state spaces of A and B respectively.

Separable (or factored) and entangled states

Consider a composite quantum system with state space $\mathcal{H}_{AB} = \mathcal{H}_A \otimes \mathcal{H}_B$.

Definition. A pure state $\psi_{AB} \in \mathcal{H}_{AB}$ is called separable if there exist $\psi_A \in \mathcal{H}_A$ and $\psi_B \in \mathcal{H}_B$ such that

$$\psi_{AB} = \psi_A \otimes \psi_B.$$

Otherwise, it is called entangled. The quantity of entanglement of a state can be measured by entropies of reduced density matrices.

Entangled states exhibit correlations that have no classical analogue. For this reason, they can be used to certify the principles of quantum mechanics, and also play key roles in quantum information and quantum computing.

Composite quantum systems

If a system can be decomposed into two *indistinguishable* quantum subsystems A and A, then the state space of this system is

$$\mathcal{H}_{AA} = \left| \begin{array}{lll} \mathcal{H}_A \vee \mathcal{H}_A & \text{(symmetrized tensor product)} & \text{if } A \text{ is a boson}, \\ \mathcal{H}_A \wedge \mathcal{H}_A & \text{(antisymmetrized tensor product)} & \text{if } A \text{ is a fermion}, \end{array} \right.$$

where $\mathcal{H}_A$ is the state space of A.

According to the spin-statistics theorem,

- **bosons are quantum objects with integer spins,**
- **fermions are quantum objects with half-integer spins.**

The definition and quantification of entanglement for composite systems made of identical bosons or identical fermions is still a field of research.

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):** $\mathcal{H} = L^2(\mathbb{R}^3,\mathbb{C}) \vee L^2(\mathbb{R}^3,\mathbb{C})$

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

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

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

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 $m_1, \cdots, m_N$ subjected to an external potential $V_{\rm ext}(\mathbf{r})$ and pair-interaction potentials $W_{ij}(\mathbf{r}_i, \mathbf{r}_j)$.

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

  $|\Psi(t, \mathbf{r}_1, \cdots, \mathbf{r}_N)|^2$**: 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**

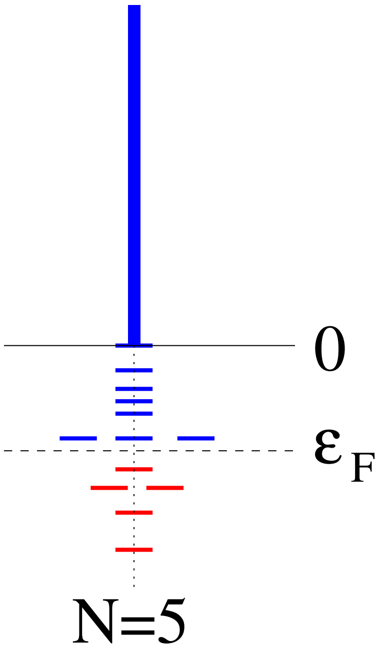
$$\left(-\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V_{\rm ext}(\mathbf{r}_i) + \sum_{1 \le i < j \le N} W_{ij}(\mathbf{r}_i, \mathbf{r}_j) \right) \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = E\, \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$\longrightarrow$ **3N-dimensional linear ellipic eigenvalue problem**

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

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

$$\begin{cases} \mathfrak{h}\,\phi_i = \varepsilon_i \phi_i, \qquad \varepsilon_1 \le \varepsilon_2 \le \cdots \le \varepsilon_N \\ \displaystyle\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij} \\ \mathfrak{h} = -\dfrac{\hbar^2}{2m}\Delta + V_{\rm ext} \end{cases}$$



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

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

The pure-state formalism presented so far is not always sufficient:

- **when a N-particle system is confined in a cavity and may exchange energy with its environment, it is in general not in a pure state, but in a mixed state represented by a density matrix**

$$\Gamma(t) = \sum_{i=1}^{+\infty} n_i(t) |\psi_i(t)\rangle\langle\psi_i(t)|, \quad \langle\psi_i(t)|\psi_j(t)\rangle = \delta_{ij}, \quad 0 \le n_i(t) \le 1, \quad \sum_{i=1}^{+\infty} n_i(t) = 1.$$

  At thermal equilibrium at temperature T, the state of the system is

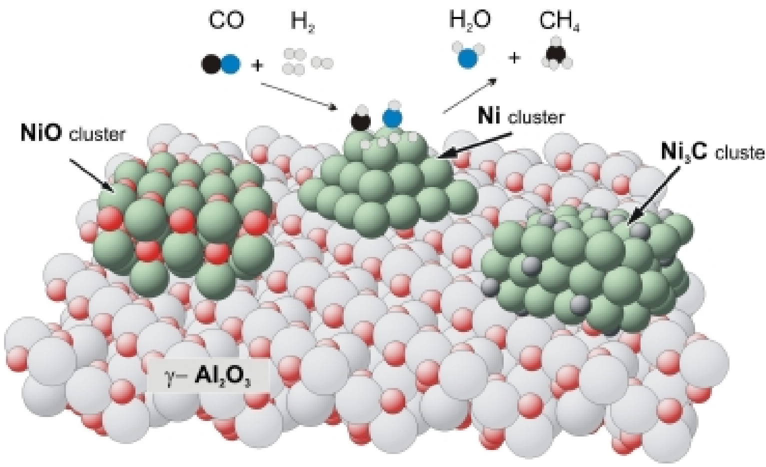
$$\Gamma = Z^{-1}\ \exp\left(-\beta H\right) \quad \textbf{where} \quad Z = \textbf{Tr}\left(\exp\left(-\beta H\right)\right) \quad \textbf{and} \quad \beta = \frac{1}{k_{\rm B}T}.$$

  The set $\mathcal{K}_N$ of N-body density matrices is a weakly-$*$ closed bounded convex subset $\mathcal{B}(\mathcal{H}_N)$ and the pure states are the extreme points of $\mathcal{K}$;

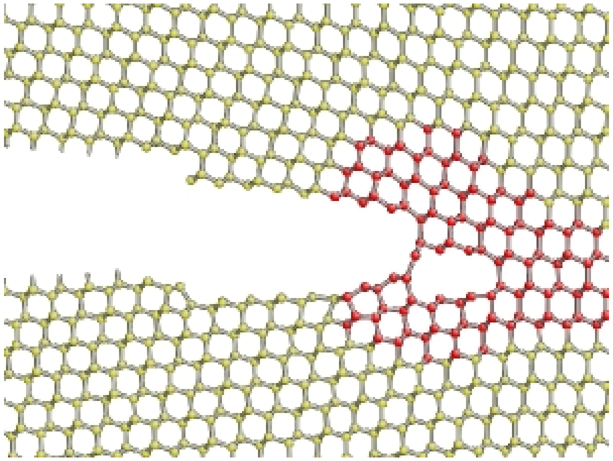
- **when the system may exchange particles with its environment, or when particles can be created or destroyed, N-particle state spaces must be replaced by Fock spaces;**

- **when the system contains infinitely many-particles (e.g. disordered crystals), states can be conveniently described in terms of suitable linear forms on the C*-algebra of admissible observables.**

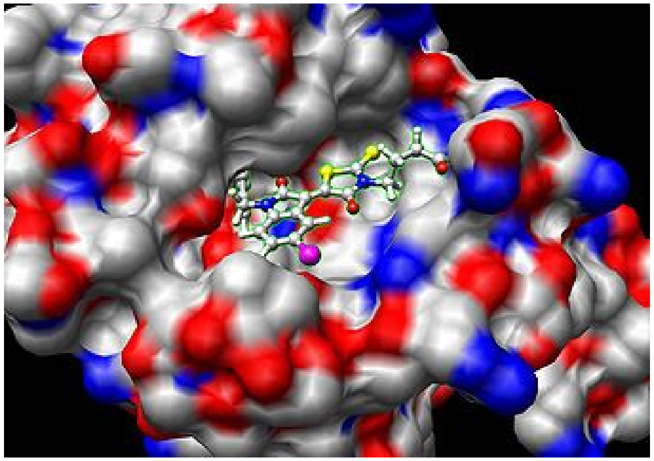
2 - First-principle molecular simulation (mathematical viewpoint)



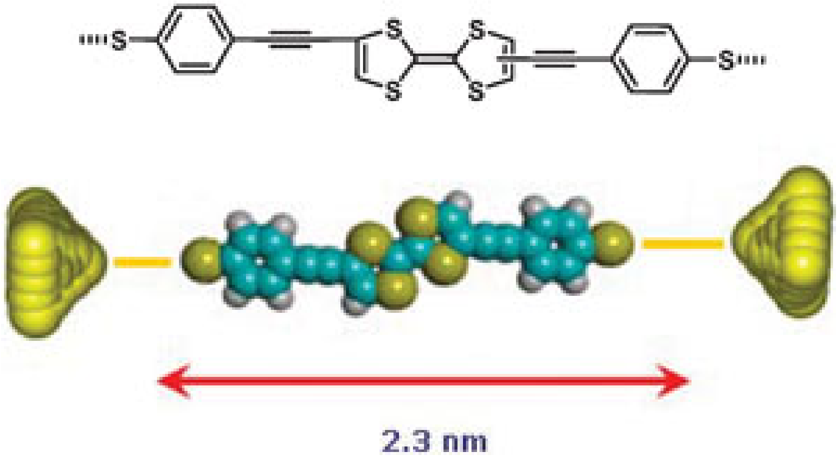
Chemistry



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:**

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

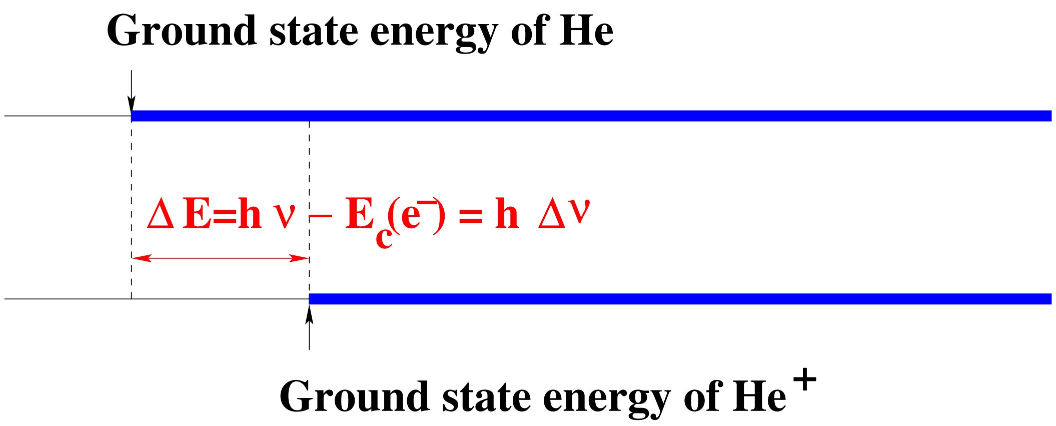
Atomic units: $\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\varepsilon_0 = 1.$

- **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):

$$\mathrm{He} + h\nu \rightarrow \mathrm{He}^{+} + e^{-}$$



Ground state energy of He

$\Delta E = h\nu - E_c(e^-) = h\,\Delta\nu$

Ground state energy of He^+

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

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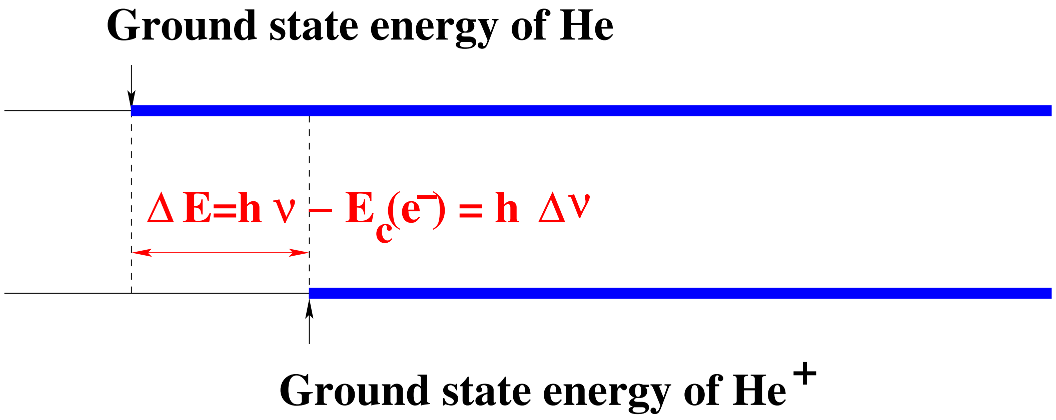

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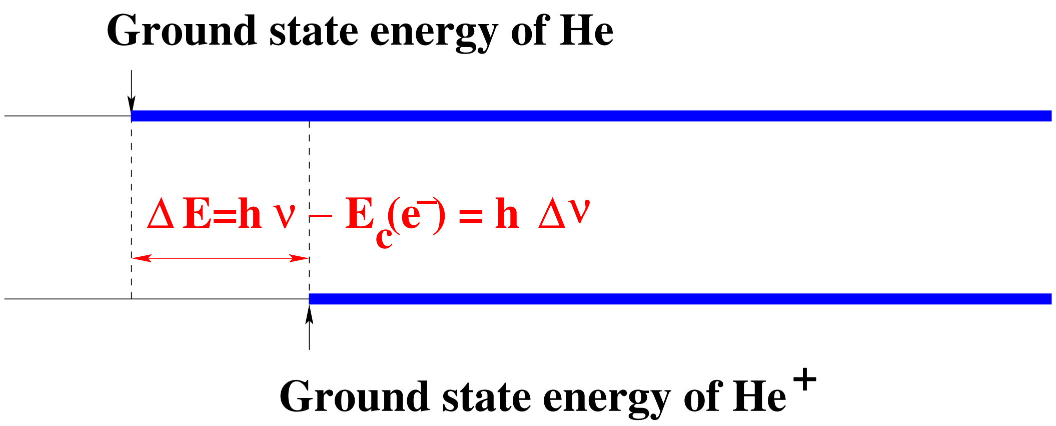


exp. : 5 945 204 238 MHz ('97)

5 945 204 356 MHz ('98)

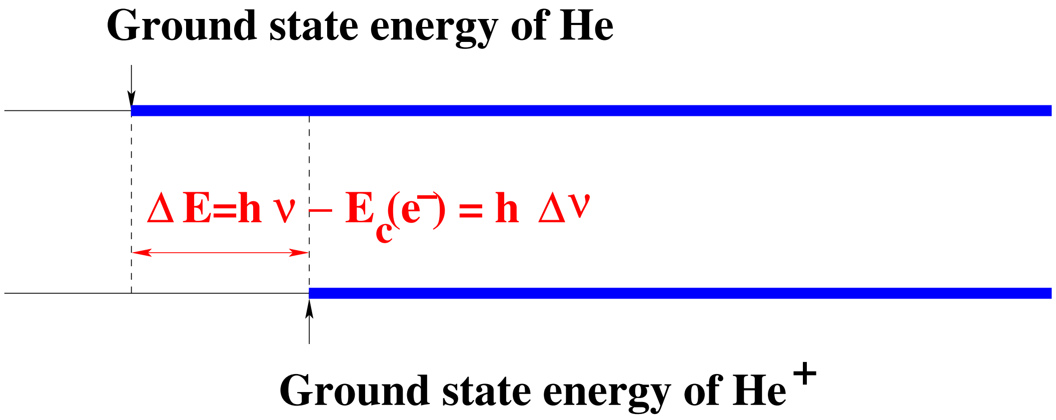
calc.: 5 945 262 288 MHz

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

$$H_{\mathrm{He}^+} = -\frac{1}{2m}\Delta_{\mathbf{R}} - \frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|}, \qquad m = 7294.29953\cdots \ \textbf{a.u.}$$

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

$$\mathrm{He} + h\nu \;\rightarrow\; \mathrm{He}^{+} + e^{-}$$



exp. : 5 945 204 238 MHz (’97)
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calc.: 5 945 262 288 MHz
5 945 204 223 MHz (R.C.)

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

Example: computation of some properties of the water molecule (H_2O)

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

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

The only parameters of these models are

- **a few fundamental constants of physics (atomic units)**

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

  $c \simeq 137.0359996287515..., \quad k_{\rm B} = 3.16681537... \times 10^{-6}$

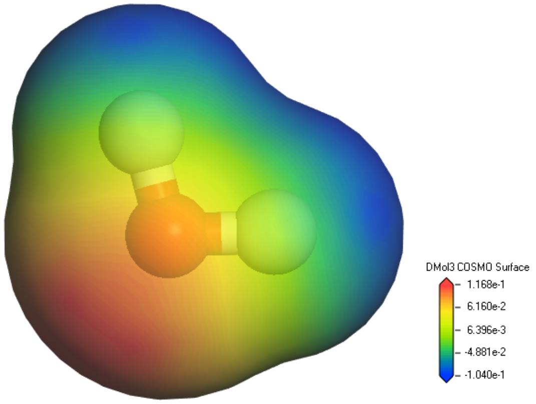
- **the charges and masses of the hydrogen and oxygen (16) nuclei**

  $z_{\rm H} = 1, \quad z_{\rm O} = 8, \quad m_{\rm H} = 1836.152701..., \quad m_{^{16}{\rm O}} = 29156.944123...$

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

- **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 $\{\mathrm{R}_k\}_{1\leq k\leq M}$



Ex: water molecule $\mathbf{H_2O}$

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

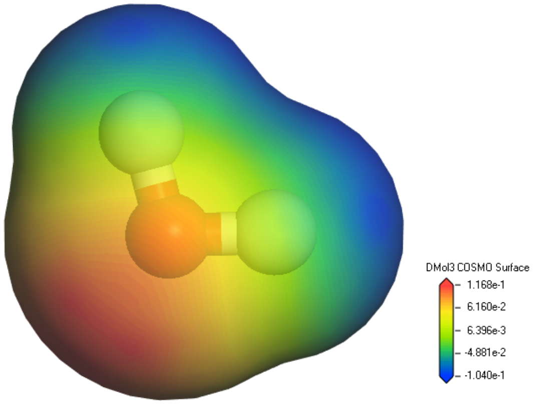
$$V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|}$$

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

$|\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)|^2$ **probability density of observing electron 1 at** r_1**, electron 2 at** r_2**, ...**

Warning: in this lecture, spin is omitted for simplicity

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



Ex: water molecule $\mathbf{H_2O}$

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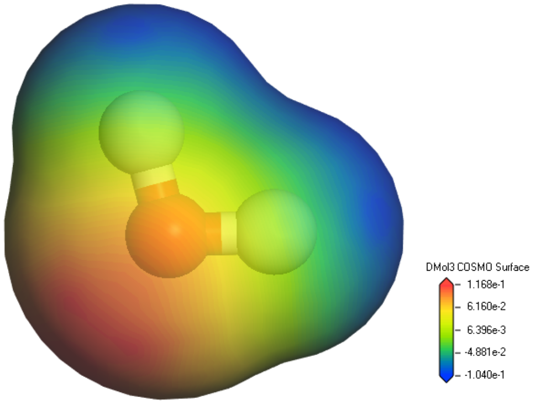
$$V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}-\mathbf{R}_k|}$$

$$\boxed{\left(-\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r}_i) + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right)\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N) = E\,\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)}$$

$|\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)|^2$ **probability density of observing electron 1 at r_1, electron 2 at r_2, ...**

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

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



Ex: water molecule H$_2$O

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

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

$$\boxed{\left(-\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V^{\rm ne}_{\{\mathbf{R}_k\}}(\mathbf{r}_i) + \sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right)\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N) = E\,\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)}$$

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

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

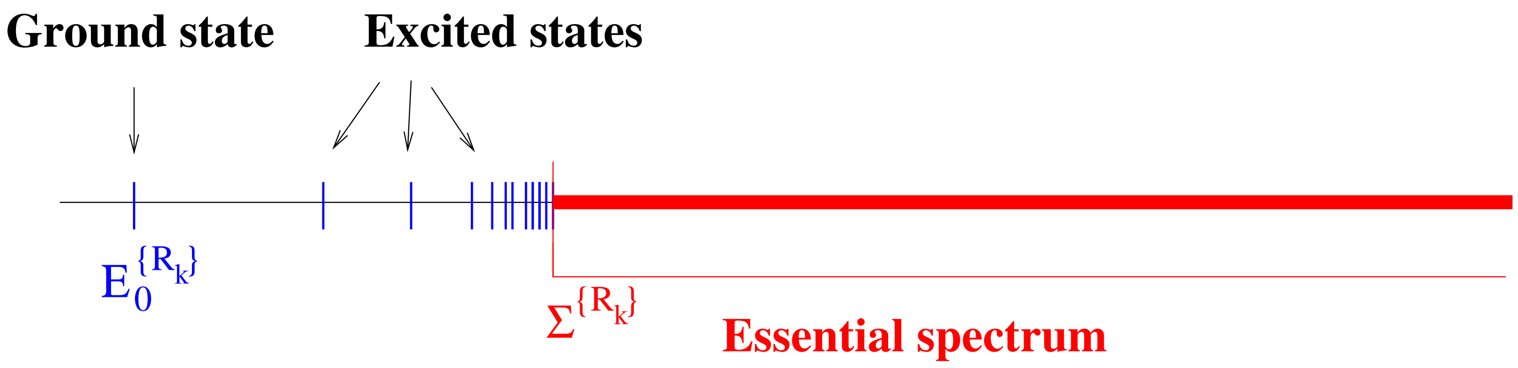
Spectrum of the electronic hamiltonian

$$H_N^{\{\mathbf{R}_k\}} = -\sum_{i=1}^{N} \frac{1}{2}\Delta_{\mathbf{r}_i} - \sum_{i=1}^{N} V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \textbf{on} \quad \mathcal{H}_N := \bigwedge^{N} L^2(\mathbb{R}^3, \mathbb{C})$$

(Pauli principle)

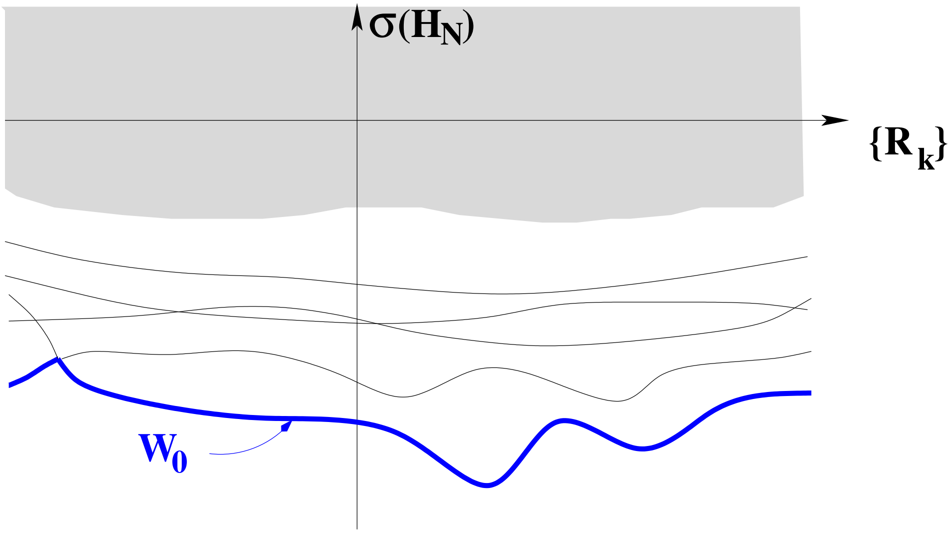
Zhislin's theorem: **if** $N \leq \sum_{k=1}^{M} z_k$ **(neutral or positively charged system), then**

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

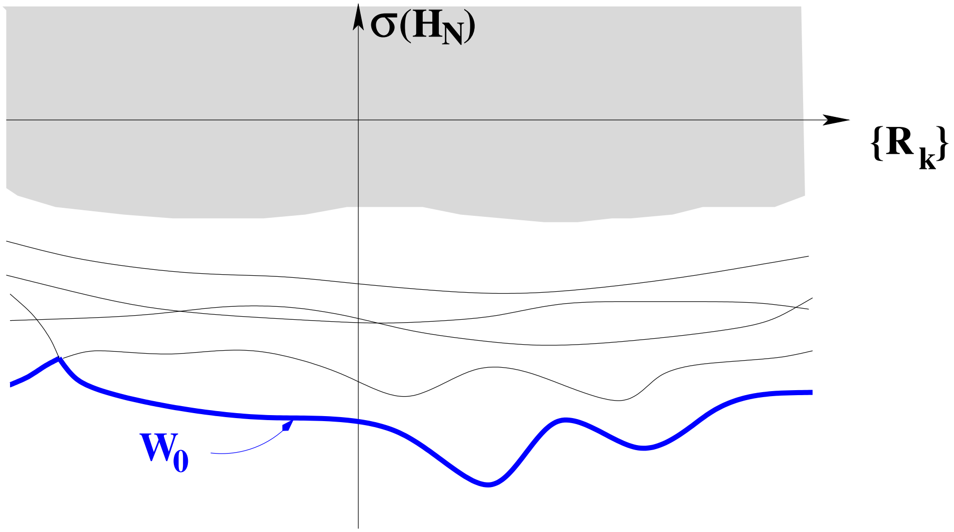


Step 1: definition of the potential energy surfaces

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



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: $\hbar \to 0$

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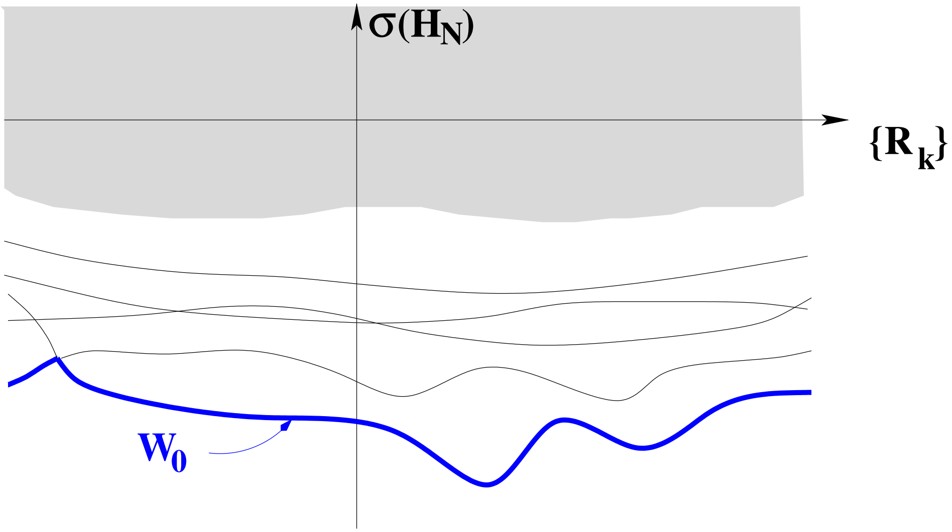
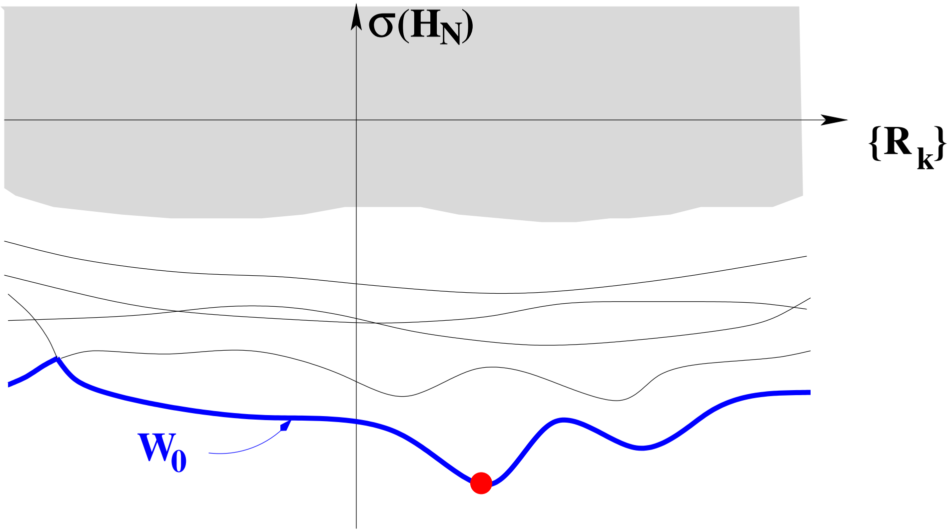


First-principle molecular dynamics

$$\boxed{m_k \frac{d^2\mathbf{R}_k}{dt^2}(t) = -\nabla_{\mathbf{R}_k} W_0(\mathbf{R}_1(t),\cdots,\mathbf{R}_M(t)), \qquad 1 \le k \le M}$$

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



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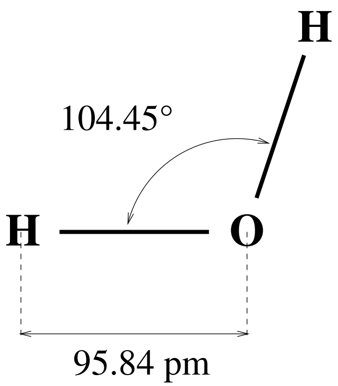
Global minima of W_0: equilibrium configurations of the system



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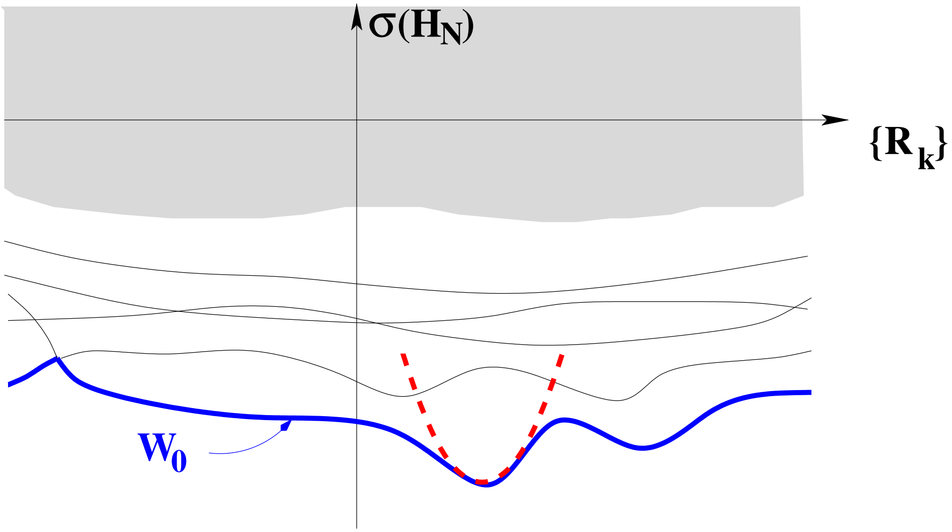

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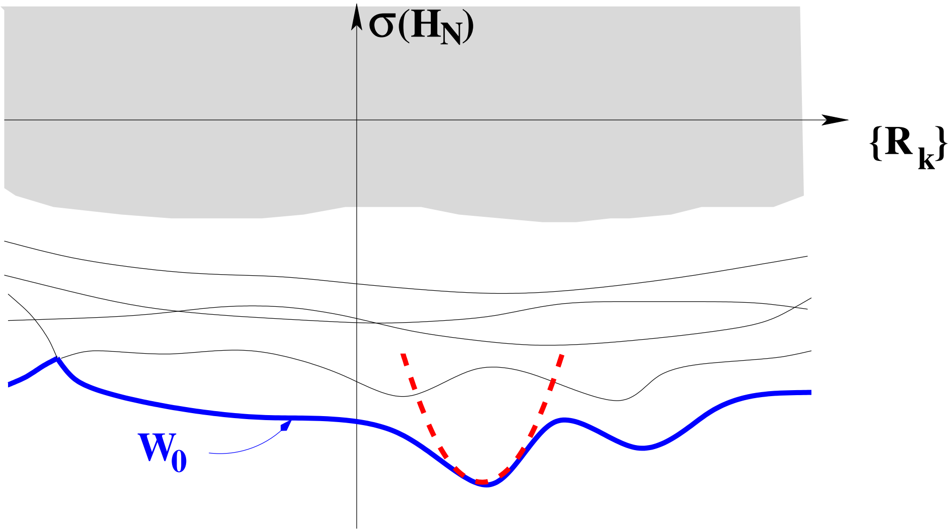
Vibration frequencies (harm. approx.)

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

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

Step 2: analysis of the potential energy surfaces



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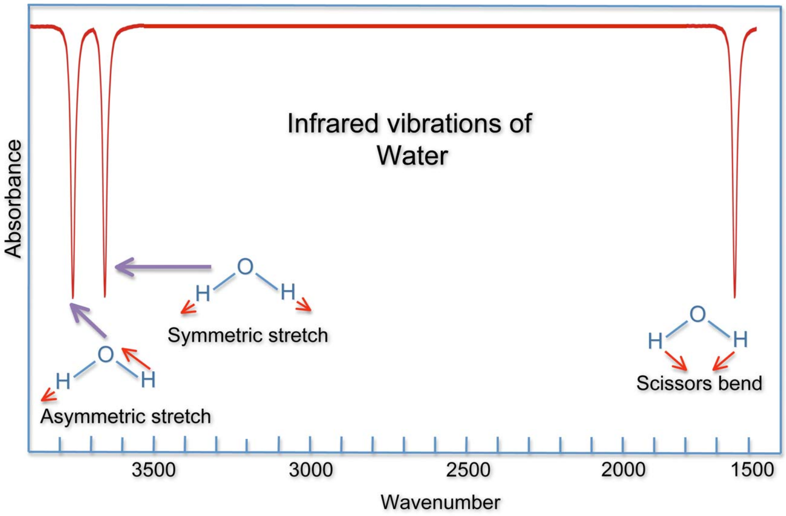
$\rightarrow$ **infrared spectrum**



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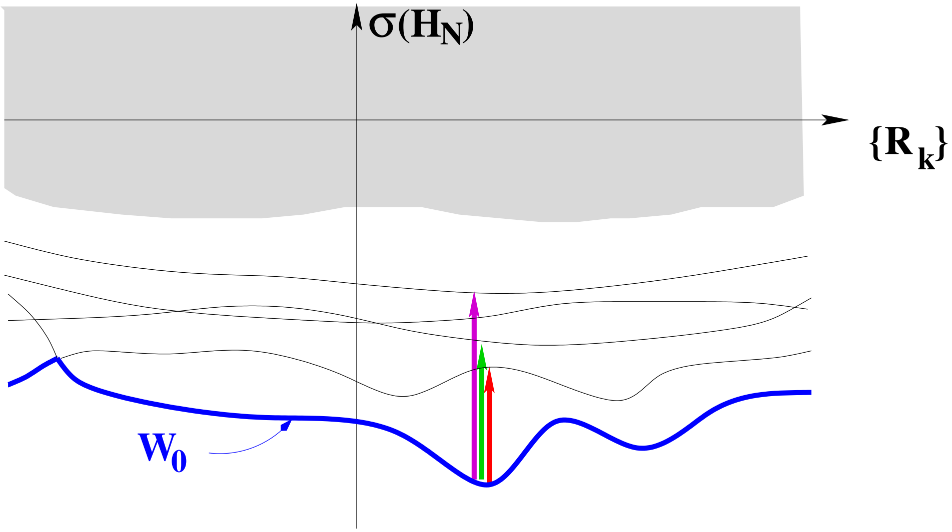
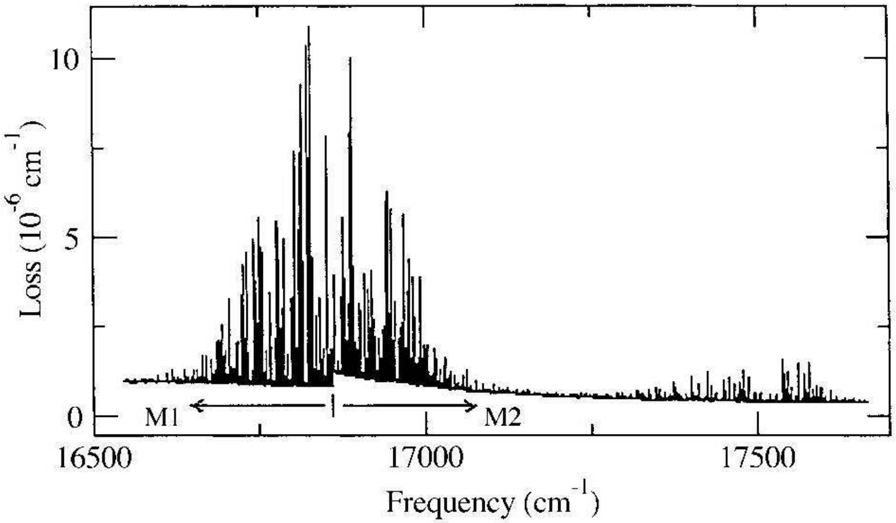


Vertical transition energies:

visible spectrum (color)
ultraviolet spectrum
X spectrum
ionization energy



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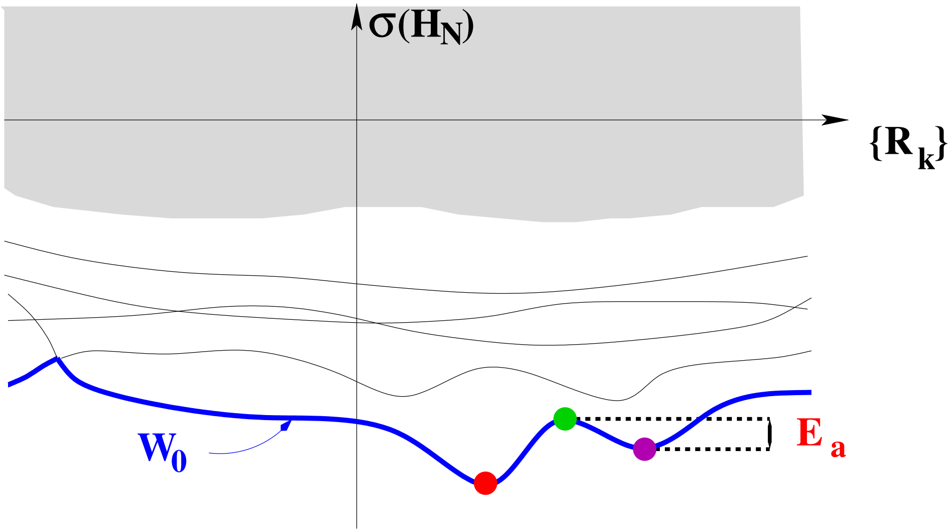

Local minima: (meta)stable states (reactants and products)

Critical points of W_0 with Morse index 1: transition states

OH + H $\to$ H_2O

$$k_{\rm TST} = \frac{\prod_{i=1}^{3N-6} \nu_i^{\rm Re}}{\prod_{i=1}^{3N-7} \nu_i^{\rm TS,+}} \, e^{-E_{\rm a}/k_{\rm B}T}$$

(large deviation theory).

Main practical issue: compute the ground state electronic energy and density for a given nuclear configuration.

- N–body electronic Schrödinger equation
  - Wavefunction methods
    - Hartree–Fock
    - Single–reference methods: MPn, CI, CC, ...
    - Multi–reference methods: MCSCF, MRCC, ...
  - Density functional theory (DFT)
    - Thomas–Fermi (orbital free) : TF, TFW, ...
    - Kohn–Sham : Hartree, $X\alpha$, LDA, GGA, ...
  - Quantum Monte Carlo
    - Variational MC
    - Diffusion MC

For brevity, we restrict ourselves to

- Hartree-Fock and Kohn-Sham (mean-field, one-particle effective models);
- single reference 2nd order methods: MP2, CISC, CCSD.

3 - Representation of electronic states

Reduced density matrix and p-body densities

The wavefunction Ψ (resp. the density matrix Γ) contains all the information about the state. This is way too much for practical applications!

p-body reduced density matrix (p-RDM) associated with $\Psi \in \mathcal{H}_N$

$$\gamma_{p,\Psi}(\mathbf{r}_1,\cdots,\mathbf{r}_p;\mathbf{r}'_1,\cdots,\mathbf{r}'_p)$$
$$= \binom{N}{p} \int_{\mathbb{R}^{3(N-p)}} \Psi(\mathbf{r}_1,\cdots,\mathbf{r}_p,\mathbf{r}_{p+1},\cdots,\mathbf{r}_N)\Psi(\mathbf{r}'_1,\cdots,\mathbf{r}'_p,\mathbf{r}_{p+1},\cdots,\mathbf{r}_N)^*\,d\mathbf{r}_{p+1}\cdots d\mathbf{r}_N$$

$\gamma_{p,\Psi}$ should be seen as the integral kernel of a bounded self-adjoint linear operator $\gamma_{p,\Psi} : \mathcal{H}_p \to \mathcal{H}_p$, called the p-RDO associated Ψ.

p-body density associated with a wavefunction $\Psi \in \mathcal{H}_N$

$$\rho_{p,\Psi}(\mathbf{r}_1,\cdots,\mathbf{r}_p) = \gamma_{p,\Psi}(\mathbf{r}_1,\cdots,\mathbf{r}_p;\mathbf{r}_1,\cdots,\mathbf{r}_p)$$

p-RDO associated with mixed states

$$\Gamma = \sum_{i=1}^{+\infty} n_i |\Psi_i\rangle\langle\Psi_i| \quad \mapsto \quad \gamma_{p,\Gamma} = \sum_{i=1}^{+\infty} n_i \gamma_{p,\Psi_i}$$

(linear map!)

Key properties of reduced density matrices and p-body densities

- **Expectation values of non-local (resp. local) p-body observables can be computed from the p-RDM (resp. the p-body density). In particular,**

$$\langle\Psi|H_N^{\{\mathbf{R}_k\}}|\,\Psi\rangle = \mathbf{Tr}\left(-\frac{1}{2}\Delta\gamma_{1,\psi}\right)+\int_{\mathbb{R}^3}\rho_{1,\Psi}V^{\mathrm{ne}}_{\{\mathbf{R}_k\}}+\frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho_{2,\Psi}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2.$$

- **If Ψ is the Slater determinant of orthonormal orbitals $(\phi_1,\cdots,\phi_N)$, then**

$$\gamma_{1,\Psi}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i(\mathbf{r}')^*,$$

  and all the $\gamma_{p,\Psi}$, $\rho_{p,\Psi}$ are simple functions of $\gamma_{1,\Psi}$. In particular,

$$\rho_{1,\Psi}(\mathbf{r}) = \gamma_{1,\Psi}(\mathbf{r},\mathbf{r}) \quad \textbf{and} \quad \rho_{2,\Psi}(\mathbf{r}_1,\mathbf{r}_2) = \rho_{1,\Psi}(\mathbf{r}_1)\rho_{1,\Psi}(\mathbf{r}_2)-|\gamma_{1,\Psi}(\mathbf{r}_1,\mathbf{r}_2)|^2.$$

Unfortunately, no practical characterization of the sets

$$\{(\gamma_1,\rho_2)\mid \exists\Psi\in\mathcal{H}_N \textbf{ s.t. } \gamma_1=\gamma_{1,\Psi},\ \rho_2=\rho_{2,\Psi}\}$$
$$\{(\gamma_1,\rho_2)\mid \exists\Gamma\in\mathcal{K}_N \textbf{ s.t. } \gamma_1=\gamma_{1,\Gamma},\ \rho_2=\rho_{2,\Gamma}\}$$

is available for numerical simulation (N-representability problem).

Discretization of the (spinless) one-electron state space

One-electron wavefunctions are usually discretized

- **either in atomic orbitals (quantum chemistry: $\mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C})$)**
- **or in planewaves (solid state physics and materials science: $\mathcal{H}_1 = L^2_{\rm per}(\Gamma, \mathbb{C})$).**

Other discretization methods include grid, finite-element, wavelets, and discontinuous Galerkin methods.

In both atomic orbitals (AO) and planewave (PW) methods, one-electron wavefunctions are expanded in a basis $\chi = (\chi_1, \cdots, \chi_{N_b}) \subset (\mathcal{H}_1)^{N_b}$ as

$$\phi(\mathbf{r}) = \sum_{\mu=1}^{N_b} \alpha_\mu \chi_\mu(\mathbf{r})$$

where, typically,

- $N_b \sim 2N - 10N$ **for AO basis sets (depending on the nuclear coord.);**
- $N_b \sim 100N - 1000N$ **for PW basis sets,**

N **being the number of electrons in the system (in the simulation cell for PW).**

Representation of discretized Hartree-Fock and Kohn-Sham states

Let $\chi = (\chi_1, \cdots, \chi_{N_b})$ be the chosen discretization basis of $\mathcal{H}_1$ and

$$\mathcal{H}_1^\chi := \text{Span}(\chi_1, \cdots, \chi_{N_b}).$$

Discretized HF and KS states are Slater det. build with orbitals from $\mathcal{H}_1^\chi$

$$\left((\phi_1, \cdots, \phi_N) \in (\mathcal{H}_1^\chi)^N, \ \int \phi_i \phi_j^* = \delta_{ij} \right) \quad \Leftrightarrow \quad \left(\phi_i(\mathbf{r}) = \sum_{\mu=1}^{N_b} C_{\mu i} \chi_\mu(\mathbf{r}), \ C^* S^\chi C = I_N \right)$$

where S^χ is the overlap matrix of the basis $\chi = (\chi_1, \cdots, \chi_{N_b})$:

$$S_{\mu\nu}^\chi = \int \chi_\mu^* \chi_\nu$$

Important remark: for any unitary matrix $U \in U(N)$, C and CU give rise to the same wavefunction Ψ (properties of Slater determinants). They therefore represent the same state. This is related to the fact that

$$\gamma_{1,\Psi}(\mathbf{r}, \mathbf{r}') = \sum_{\mu,\nu=1}^{N_b} D_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})^* \quad \textbf{with} \quad D = CC^*.$$

Orbital vs density matrix formulation of HF and KS problems

$$
\begin{aligned}
E_{0,\chi}^{\{\mathbf{R}_k\},\mathrm{HF/KS}} &= \inf\left\{ E_\chi^{\{\mathbf{R}_k\},\mathrm{HF/KS}}(CC^*), \quad C \in \mathbb{C}^{N_b \times N}, \; C^* S^\chi C = I_N \right\} \\
&= \inf\left\{ E_\chi^{\{\mathbf{R}_k\},\mathrm{HF/KS}}(D), \quad D \in \mathbb{C}^{N_b \times N_b}, \; D^* = D = D S^\chi D, \; \mathbf{Tr}(S^\chi D) = N \right\}
\end{aligned}
$$

$$
E_\chi^{\{\mathbf{R}_k\},\mathrm{HF}}(D) = \underset{\substack{\uparrow \\ \textbf{linear}}}{\mathbf{Tr}(h^{\{\mathbf{R}_k\},\chi} D)} + \frac{1}{2}\underset{\substack{\uparrow \\ \textbf{quadratic}}}{\mathbf{Tr}(G^\chi(D) D)}
$$

$$
E_\chi^{\{\mathbf{R}_k\},\mathrm{KS}}(D) = \underset{\substack{\uparrow \\ \textbf{linear}}}{\mathbf{Tr}(h^{\{\mathbf{R}_k\},\chi} D)} + \frac{1}{2}\underset{\substack{\uparrow \\ \textbf{quadratic}}}{\mathbf{Tr}(J^\chi(D) D)} + \underset{\substack{\uparrow \\ \textbf{nonlinear}}}{E_\chi^{\mathrm{xc}}(D)}
$$

Core Hamiltonian matrix: $h_{\mu\nu}^{\{\mathbf{R}_k\},\chi} = \frac{1}{2}\int_{\mathbb{R}^3} \nabla \chi_\mu^* \cdot \nabla \chi_\nu - \sum_{k=1}^{M} z_k \int_{\mathbb{R}^3} \frac{\chi_\mu(\mathbf{r})^* \chi_\nu(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} \, d\mathbf{r}$

The set of discretized HF and KS states in the basis $\chi = (\chi_1, \cdots, \chi_{N_b})$ is therefore diffeomorphic to

$$\mathcal{S}_N^\chi / U(N) \quad \equiv \quad \mathcal{G}_N^\chi$$

where $\mathcal{S}_N^\chi$ and $\mathcal{G}_N^\chi$ respectively denote the Stiefel and Grassmann manifolds

$$\mathcal{S}_N^\chi = \left\{ C \in \mathbb{C}^{N_b \times N} \mid C^* S^\chi C = I_N \right\},$$
$$\mathcal{G}_N^\chi = \left\{ D \in \mathbb{C}^{N_b \times N_b} \mid D^* = D = D S^\chi D, \ \mathbf{Tr}\left(S^\chi D \right) = N \right\}.$$

Remarks:

- **the manifolds $\mathcal{S}_N^\chi / U(N)$ and $\mathcal{G}_N^\chi$ have the same dimension $N(N_b - N)$;**
- **from a geometrical point of view, the Grassmann manifold $\mathcal{G}_N^\chi$ is the submanifold of $\mathcal{L}(\mathbb{C}^{N_b})$ consisting of the rank-N orthogonal projectors when $\mathbb{C}^{N_b}$ is endowed with the scalar product defined by S^χ (and therefore with the canonical inner product when the basis χ is orthonormal);**
- **when both the basis set functions χ_j and the orbitals are real-valued, the result holds with $\mathbb{C}$ replaced with $\mathbb{R}$ and $U(N)$ replaced by $O(N)$, the group of real orthogonal matrices.**

Exponential map

The manifold $\mathcal{G}_N^\chi$ is a nonlinear object. It can however be parametrized in the following way: a reference density matrix $D_0 \in \mathcal{G}_N^\chi$ being given, the "exponential map"

$$\begin{aligned} f : \mathbb{C}^{N\times(N_b-N)} &\to \mathcal{G}_N^\chi \\ A &\mapsto f(A) = (S^\chi)^{-\frac{1}{2}} \exp\begin{pmatrix} 0_N & -A \\ A^* & 0_{N_b-N} \end{pmatrix} (S^\chi)^{\frac{1}{2}} D_0 (S^\chi)^{\frac{1}{2}} \exp\begin{pmatrix} 0_N & A \\ -A^* & 0_{N_b-N} \end{pmatrix} (S^\chi)^{-\frac{1}{2}} \end{aligned}$$

defines a local chart of $\mathcal{G}_N^\chi$ centered at $f(0) = D_0$.

Note that f is surjective but not injective.

Discretized of N-body wavefunctions and p-RDOs

If $\Psi \in \mathcal{H}_N^\chi$, then $\gamma_{p,\Psi}|_{\mathcal{H}_p^\chi} : \mathcal{H}_p^\chi \to \mathcal{H}_p^\chi$ and

$$\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \sum_{1\leq\kappa_1<\cdots<\kappa_N\leq N_b} c_{\kappa_1,\cdots,\kappa_N} \left(\chi_{\kappa_1} \wedge \cdots \wedge \chi_{\kappa_N}\right)(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$$\gamma_{p,\Psi} = \sum_{\substack{1 \leq \mu_1 < \cdots < \mu_p \leq N_b \\ 1 \leq \nu_1 < \cdots < \nu_p \leq N_b}} D^{(p)}_{\mu_1,\cdots,\mu_p;\nu_1,\cdots,\nu_p} |\chi_{\mu_1} \wedge \cdots \wedge \chi_{\mu_p}\rangle\langle\chi_{\nu_1} \wedge \cdots \wedge \chi_{\nu_p}|.$$

Discretized 1-body density matrix: if $\Psi \in \mathcal{H}_N^\chi$, then

$$\gamma_{1,\Psi}(\mathbf{r}, \mathbf{r}') = \sum_{\mu,\nu=1}^{N_b} D_{\mu,\nu}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}')^*,$$

with

$$D \in \mathbb{C}^{N_b\times N_b}, \quad D^* = D, \quad 0 \leq DS^\chi D \leq D, \quad \mathbf{Tr}(S^\chi D) = N.$$

and $DS^\chi D = D$ if and only if Ψ is a Slater determinant.

Second quantization formalism

- **Fock space**

$$\mathbb{F} := \bigoplus_{N=0}^{+\infty} \mathcal{H}_N, \qquad \mathcal{H}_0 = \mathbb{C}, \qquad \mathcal{H}_1 = L^2(\mathbb{R}^3, \mathbb{C}), \qquad \mathcal{H}_N = \bigwedge^N \mathcal{H}_1.$$

- **Annihilation and creation operators**

$$\forall \phi \in \mathcal{H}_1, \qquad a(\phi) : \mathcal{H}_N \to \mathcal{H}_{N-1}, \qquad a^\dagger(\phi) : \mathcal{H}_N \to \mathcal{H}_{N+1}, \qquad a^\dagger(\phi) = (a(\phi))^*,$$

$$\forall \Psi_N \in \mathcal{H}_N, \qquad (a(\phi)\Psi_N)(\mathbf{r}_1, \cdots, \mathbf{r}_{N-1}) = \sqrt{N} \int_{\mathbb{R}^3} \overline{\phi(\mathbf{r})}\, \Psi_N(\mathbf{r}, \mathbf{r}_1, \cdots, \mathbf{r}_{N-1})\, d\mathbf{r}.$$

$$a \in \mathcal{A}(\mathcal{H}_1, \mathcal{B}(\mathbb{F})), \qquad a^\dagger \in \mathcal{B}(\mathcal{H}_1, \mathcal{B}(\mathbb{F})),$$

Note that if $\phi \in \mathcal{H}_1^\chi$ **and** $\Psi_N \in \mathcal{H}_N^\chi$**, then** $a(\phi)\Psi_N \in \mathcal{H}_{N-1}^\chi$ **and** $a^\dagger(\phi)\Psi_N \in \mathcal{H}_{N+1}^\chi$**.**

Discretized N-electron state spaces and Fock space

Let $\chi = (\chi_1, \cdots, \chi_{N_b})$ be the chosen discretization basis of $\mathcal{H}_1$ and

$$\mathcal{H}_1^\chi := \text{Span}(\chi_1, \cdots, \chi_{N_b}).$$

- **The discrete N-electron state space is then defined for all $1 \leq N \leq N_b$ as**

  $$\mathcal{H}_N^\chi := \bigwedge^N \mathcal{H}_1^\chi \quad \textbf{and} \quad \dim(\mathcal{H}_N^\chi) = \begin{pmatrix} N_b \\ N \end{pmatrix}$$ ⟶ **curse of dimensionality!**

  A (non-orthogonal in general) basis of $\mathcal{H}_N^\chi$ is

  $$\psi_{\mu_1,\mu_2,\cdots,\mu_N}(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}}\det(\chi_{\mu_i}(\mathbf{r}_j)), \quad 1 \leq \mu_1 < \mu_2 < \cdots < \mu_N \leq N_b.$$

- **The corresponding discretization of the Fock space $\mathcal{F} := \bigoplus_{N=0}^{+\infty} \mathcal{H}_N$ then is**

  $$\mathcal{F}^\chi := \bigoplus_{N=0}^{N_b} \mathcal{H}_N^\chi, \quad \textbf{with} \quad \mathcal{H}_0^\chi = \mathbb{C}, \quad \textbf{so that} \quad \dim(\mathcal{F}^\chi) = 2^{N_b}.$$

Excitations with respect to a reference Slater determinant

- **A Hartree-Fock (or Kohn-Sham) calculation in the basis set χ provides a set of N_b orthonormal molecular orbitals belonging to $\mathcal{H}_1^\chi$, among which**
  - **N occupied orbitals $(\phi_i)_{1\le i\le N}$,**
  - **$(N_b - N)$ unoccupied (or virtual) orbitals $(\phi_a)_{N+1\le a\le N_b}$.**
- **The Slater determinant constructed with the N occupied orbitals**

$$\Phi_0(\mathbf{r}_1,\cdots,\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\mathrm{det}(\phi_i(\mathbf{r}_j)) \qquad \in \mathcal{H}_N^\chi$$

  is the Hartree-Fock (or Kohn-Sham) ground state in the basis set χ.
- **Denoting by $a_{i_j} = a(\phi_{i_j})$ and $a_{a_k}^\dagger = a^\dagger(\phi_{a_k})$ the annihilation and creation operators associated with the occupied and virtual orbitals ϕ_{i_j} and ϕ_{a_k} respectively, an orthonormal basis of $\mathcal{H}_N^\chi$ is obtained by collecting:**
  - **the reference Slater determinant Φ_0;**
  - **the single-excitation Slater determinants $\Phi_{i_1}^{a_1} = a_{a_1}^\dagger a_{i_1}\Phi_0$;**
  - **the double-excitation Slater determinants $\Phi_{i_1 i_2}^{a_1 a_2} = a_{a_1}^\dagger a_{a_2}^\dagger a_{i_1} a_{i_2}\Phi_0$;**
  - **...**

Excitation operators

- **single-excitation:** $T_{i_1}^{a_1} = a_{a_1}^\dagger a_{i_1}, \quad 1 \le i_1 \le N, \quad N+1 \le a_1 \le N_b$
- **di-excitation:** $T_{i_1 i_2}^{a_1 a_2} = a_{a_1}^\dagger a_{a_2}^\dagger a_{i_1} a_{i_2}, \quad 1 \le i_1 < i_2 \le N, \quad N+1 \le a_1 < a_2 \le N_b$
- **...**

Excitation subspaces

- **single-double (SD) excitation subspaces**

$$\begin{aligned} V_2 &= \textbf{Span}\left\{I, T_{i_1}^{a_1}, T_{i_1 i_2}^{a_1 a_2}\right\} \Phi_0 && \subset \mathcal{H}_N^\chi \\ W_2 &= \textbf{Span}\left\{T_{i_1}^{a_1}, T_{i_1 i_2}^{a_1 a_2}\right\} && \subset \mathcal{B}(\mathcal{H}_N^\chi) \end{aligned}$$

- **single-double (SDT) excitation subspaces**

$$\begin{aligned} V_3 &= \textbf{Span}\left\{I, T_{i_1}^{a_1}, T_{i_1 i_2}^{a_1 a_2}, T_{i_1 i_2 i_3}^{a_1 a_2 a_3}\right\} \Psi_0 && \subset \mathcal{H}_N^\chi \\ W_3 &= \textbf{Span}\left\{T_{i_1}^{a_1}, T_{i_1 i_2}^{a_1 a_2}, T_{i_1 i_2 i_3}^{a_1 a_2 a_3}\right\} && \subset \mathcal{B}(\mathcal{H}_N^\chi) \end{aligned}$$

- **...**

Single-double configuration interaction (CISD): simple Galerkin approx.

$$\left\{\begin{array}{l}\textbf{Find } (E,\Psi)\in\mathbb{R}\times V_2 \textbf{ such that}\\ \forall\Psi'\in V_2,\ \langle\Psi'|H_N|\Psi\rangle = E\langle\Psi'|\Psi\rangle\\ \|\Psi\|=1\end{array}\right. \quad\Leftrightarrow$$

Linear eigenvalue problem of size dim$(V_2)\simeq\frac{1}{4}N^2(N_b-N)^2$

Single-double coupled-cluster (CCSD): based on the property

$$\left\{|e^T\Phi_0\rangle,\ T\in W_N\right\} = \{\Psi\in\mathcal{H}_N \mid \langle\Phi_0|\Psi\rangle = 1\}\,.$$

$$\left\{\begin{array}{l}\textbf{Find } (E,T)\in\mathbb{R}\times W_2 \textbf{ such that}\\ \forall\Psi'\in V_2,\ \langle\Psi'|H_N|e^T\Phi_0\rangle = E\langle\Psi'|e^T\Phi_0\rangle\end{array}\right.$$

$$\Updownarrow$$

$$\left\{\begin{array}{l}\textbf{Find } (E,T)\in\mathbb{R}\times W_2 \textbf{ such that}\\ \forall\Psi'\in V_2,\ \langle\Psi'|e^{-T}H_Ne^T|\Phi_0\rangle = E\langle\Psi'|\Phi_0\rangle\end{array}\right. \quad\Leftrightarrow$$

Quartic algebraic equation with dim$(W_2)\simeq\frac{1}{4}N^2(N_b-N)^2$ **real unknowns**

Take-home messages and conclusion

Relevant representation levels of quantum states

- **The wavefunction Ψ (resp. the density matrix Γ) contains all the information about the state. This is way too much for practical applications!**
- **Expectation values of non-local (resp. local) p-body observables can be computed from the p-RDM (resp. the p-body density).**

Representation of HF and KS states

- **HF and KS states are Slater determinants. After discretization in a basis set $\chi = (\chi_1, \cdots, \chi_{N-b})$, the set of HS or KS states is diffeomorphic to**

$$\mathcal{S}_N^\chi / U(N) \quad \equiv \quad \mathcal{G}_N^\chi$$

where $\mathcal{S}_N^\chi$ and $\mathcal{G}_N^\chi$ respectively denote the Stiefel and Grassmann manifolds

$$\mathcal{S}_N^\chi = \left\{ C \in \mathbb{C}^{N_b \times N} \mid C^* S^\chi C = I_N \right\},$$
$$\mathcal{G}_N^\chi = \left\{ D \in \mathbb{C}^{N_b \times N_b} \mid D^* = D = D S^\chi D, \ \mathbf{Tr}\,(S^\chi D) = N \right\}.$$

- **Note that for atomic basis sets, the overlap matrix $S^\chi_{\mu\nu} = \int \chi_\mu^* \chi_\nu$ depends on the atomic positions.**
- **The exponential map provides local charts of the manifold $\mathcal{G}_N^\chi$.**

Take-home messages and conclusion

Representation of CI and CC states

- **in the second quantization formalism, CI and CC states are represented by order-n tensors with $n = 4$ for CISD and CCSD, $n = 6$ for CISDT and CCSDT, $n = 8$ for CISDTQ, CCSDTQ, etc.**

  Ex. : for CCSD t_i^a and t_{ij}^{ab}, $1 \leq i < j \leq N$, $N + 1 \leq a < b \leq N_b$

- **low-rank tensor methods may allow one to store and manipulate these tensors at a much lower cost in terms of memory and computational time.**