Mathematical aspects of electronic structure theory

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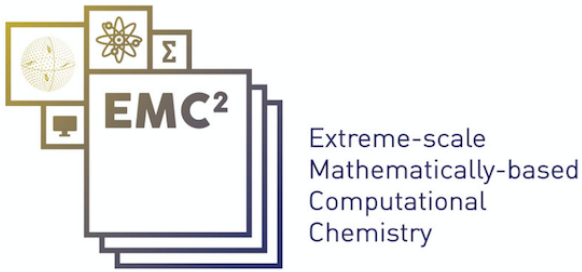


Question 1

A Fortran library for solving $A\mathbf{x} = \mathbf{b}$ gives the following results:

$$\mathbf{A} = \begin{pmatrix} 10 & 7 & 8 & 7 \\ 7 & 5 & 6 & 5 \\ 8 & 6 & 10 & 9 \\ 7 & 5 & 9 & 10 \end{pmatrix} \qquad \mathbf{b} = \begin{pmatrix} 32 \\ 23 \\ 33 \\ 31 \end{pmatrix} \qquad \textbf{Solution: } \mathbf{x} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

$$\mathbf{A} = \begin{pmatrix} 10 & 7 & 8 & 7 \\ 7 & 5 & 6 & 5 \\ 8 & 6 & 10 & 9 \\ 7 & 5 & 9 & 10 \end{pmatrix} \qquad \mathbf{b} = \begin{pmatrix} 32.001 \\ 22.999 \\ 33.001 \\ 30.999 \end{pmatrix} \qquad \textbf{Solution: } \mathbf{x} = \begin{pmatrix} 1.082 \\ 0.862 \\ 1.035 \\ 0.979 \end{pmatrix}$$

$$\mathbf{A} = \begin{pmatrix} 10 & 7.021 & 8 & 7 \\ 7 & 5 & 6 & 5 \\ 8 & 6 & 10 & 9 \\ 7 & 5 & 9 & 10 \end{pmatrix} \qquad \mathbf{b} = \begin{pmatrix} 32 \\ 23 \\ 33 \\ 31 \end{pmatrix} \qquad \textbf{Solution: } \mathbf{x} = \begin{pmatrix} -2.77\ldots \\ 7.19\ldots \\ -0.51\ldots \\ 1.90\ldots \end{pmatrix}$$

Should you trust this library?

Question 2

Constrained optimization is ubiquitous in quantum physics and chemistry (e.g. Hartree-Fock, DFT, etc.). In Physics and Chemistry textbooks, such problems are solved using the Lagrangian method.

Example: solve $\inf_{g(x)=0} E(x)$ **where** $E : \mathbb{R}^d \to \mathbb{R}$ **and** $g : \mathbb{R}^d \to \mathbb{R}^m$ **are regular.**

Introduce the Lagrangian $L : \mathbb{R}^d \times \mathbb{R}^m \to \mathbb{R}$ **defined as**

$$L(x, \lambda) = E(x) + \lambda^T g(x).$$

Then, the minimizers are obtained by solving the system of equations

$$\begin{cases} \nabla_x L(x, \lambda) = 0 \\ \\ \nabla_\lambda L(x, \lambda) = 0, \end{cases}$$

Application: $d = 1$**,** $m = 1$**,** $E(x) = x$**,** $g(x) = x^2$

$$\begin{cases} 1 + 2\lambda x = 0 \\ x^2 = 0 \end{cases} \quad \Rightarrow$$

No solution, though $x = 0$ **is obviously a minimizer!**

What's the catch?

Question 3

Diagonalizing the translation operators $(T_{\mathbf{R}})_{\mathbf{R}\in\mathbb{Z}^3}$

$$(T_{\mathbf{R}}\psi)(\mathbf{r}) = \psi(\mathbf{r}-\mathbf{R})$$

Let $\psi \neq 0$ **be such that** $T_{\mathbf{R}}\psi = C(R)\psi$ **for all** $\mathbf{R} \in \mathbb{Z}^3$ **with** $C(R) \in \mathbb{C}$**. Since**

$$|C(\mathbf{R})|^2 \int |\psi(\mathbf{r})|^2\, d\mathbf{r} = \int |C(R)\psi(\mathbf{r})|^2\, d\mathbf{r} = \int |(T_{\mathbf{R}}\psi)(\mathbf{r})|^2\, d\mathbf{r} = \int |\psi(\mathbf{r}-\mathbf{R})|^2\, d\mathbf{r}$$
$$= \int |\psi(\mathbf{r})|^2\, d\mathbf{r}, \qquad (1)$$

then $|C(R)| = 1$ **and therefore** $C(R) = e^{i\alpha(R)}$**. Since** $T_{\mathbf{R}+\mathbf{R}'} = T_{\mathbf{R}}T_{\mathbf{R}'}$**, we get** $C(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$ **for some** $\mathbf{k} \in \mathbb{R}^3$**. And from there, we get**

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) \quad \textbf{where } u \textbf{ is an } \mathbb{Z}^3\textbf{-periodic function}$$

But then, $\int |\psi(\mathbf{r})|^2\, d\mathbf{r} = +\infty$**, and we can't infer from** (1) **that** $|C(R)| = 1$**.**

How to make this (physically correct) argument mathematically correct?

Question 4

The bound states of the hydrogen atom Hamiltonian are known

$$\hat{h} = -\frac{1}{2}\Delta - \frac{1}{r} \qquad \hat{h}\,\varphi_{n,\ell,m}(r,\theta,\phi) = E_n \varphi_{n,\ell,m}(r,\theta,\phi), \qquad \left| \begin{array}{l} n \in \mathbb{N}^* \\ 0 \leq \ell \leq n-1 \\ -\ell \leq m \leq \ell \end{array} \right.$$

When two hydrogen atoms are at distance $R \gg 1$ a.u., their interaction energy can be expanded as

$$\Delta E(R) = -\frac{C_6}{R^6} + \text{h.o.t.} \quad \textbf{(van der Waals interaction)}$$

The C_6 coefficient can be computed by perturbation theory

Using the "sum over state" technique in the basis $(\varphi_{n,\ell,m})$ we get

$C_6 \simeq 3.923$ u.a. **to be compared with the correct value** $C_6 \simeq 6.499$ u.a.

What's wrong in this approach?

Question 5

Which spin states can you actually represent with your two hands?

1. **Spectral theory of self-adjoint operators**

2. **From molecules to materials**

3. **A bit of numerical analysis**

4. **Constrained optimization and Lagrange multipliers**

1 - Spectral theory of self-adjoint operators

References:

- **E.B. Davies, *Linear operators and their spectra*, Cambridge University Press 2007.**
- **B. Helffer, *Spectral theory and its applications*, Cambridge University Press 2013.**
- **M. Reed and B. Simon, *Modern methods in mathematical physics*, in 4 volumes, 2nd edition, Academic Press 1972-1980.**
- **M. Lewin, *Théorie spectrale et mécanique quantique*, Springer 2022.**

Notation: in this section, $\mathcal{H}$ denotes a separable complex Hilbert space, $\langle \cdot | \cdot \rangle$ its inner product, and $\| \cdot \|$ the associated norm.

Fundamental principles of quantum mechanics

1. **To each quantum system is associated a separable complex Hilbert space $\mathcal{H}$**

2. **If the state of the system at time t is completely known (pure state), it can be described by a normalized vector $\psi(t)$ of $\mathcal{H}$. The set of physically admissible pure states is the projective space $P(\mathcal{H})$.**

3. **Physical observables are represented by self-adjoint operators on $\mathcal{H}$.**

4. **Let a be a physical observable represented by the self-adjoint operator A. The outcome of a measurement of a is always in $\sigma(A)$, the spectrum of A.**

5. **If, just before the measurement, the system is in the pure state $\psi(t_0)$, then the probability that the outcome lays in the interval $I \subset \mathbb{R}$ is $\|\mathbb{1}_I(A)\psi(t_0)\|^2$, where $\mathbb{1}_I$ is the characteristic function of I and $\mathbb{1}_I(A)$ is defined by functional calculus.**

6. **If the system is isolated, its dynamics between two successive measures is given by $\psi(t) = U(t-t_0)\psi(t_0)$ where $U(\tau) = e^{-i\tau H/\hbar}$, H being the Hamiltonian, i.e. the self-adjoint operator associated with the energy.**

Definition (Hilbert space). **A Hilbert space is a real or complex vector space $\mathcal{H}$ endowed with a inner product $\langle\cdot|\cdot\rangle$ and complete for the associated norm $\|\cdot\|$.**

Definition (completeness). **A sequence $(\psi_n)_{n\in\mathbb{N}}$ of elements of a normed vector space $(\mathcal{H}, \|\cdot\|)$ is Cauchy if**

$$\forall \varepsilon > 0, \quad \exists N \in \mathbb{N} \quad \textbf{s.t.} \quad \forall q \geq p \geq N, \quad \|\psi_p - \psi_q\| \leq \varepsilon.$$

The normed vector space $(\mathcal{H}, \|\cdot\|)$ is called complete if any Cauchy sequence of elements of $\mathcal{H}$ converges in $\mathcal{H}$.

Example: all finite-dimensional normed $\mathbb{R}$- or $\mathbb{C}$-vector spaces are complete.

- **Endowed with the hermitian inner product, $\mathbb{C}^d$ is a Hilbert space:**

$$\langle \mathbf{x}|\mathbf{y}\rangle = \sum_{1\leq i\leq d} \overline{x_i}\, y_i, \qquad \|\mathbf{x}\| = \langle \mathbf{x}|\mathbf{s}\rangle^{1/2} = \left(\sum_{1\leq i\leq d} |x_i|^2\right)^{1/2}.$$

- **Let $S \in \mathbb{C}^{d\times d}$ be a positive definite hermitian matrix ($S_{ji} = \overline{S_{ij}}$ for all $1 \leq i, j \leq d$ and $\mathbf{x}^* S\mathbf{x} > 0$ for all $\mathbf{x} \in \mathbb{C}^d \setminus \{0\}$). Then $\langle \mathbf{x}|\mathbf{y}\rangle_S = \mathbf{x}^* S\mathbf{y}$ defines a inner product on $\mathbb{C}^d$ and**

$$\forall \mathbf{x} \in \mathbb{C}^d, \quad \lambda_1(S)\|\mathbf{x}\| \leq \|\mathbf{x}\|_S \leq \lambda_d(S)\|\mathbf{x}\|,$$

where $\lambda_1(S) \leq \lambda_2(S) \leq \cdots \leq \lambda_d(S)$ are the eigenvalues of S.

Fundamental examples: the Hilbert space $L^2(\mathbb{R}^d, \mathbb{C})$.

- **The sequilinear form**

$$\langle \varphi | \psi \rangle := \int_{\mathbb{R}^d} \overline{\varphi} \psi := \int_{\mathbb{R}^d} \overline{\varphi(\mathbf{r})}\, \psi(\mathbf{r})\, d\mathbf{r}$$

defines a inner product on

$$C_{\mathrm{c}}^{\infty}(\mathbb{R}^d, \mathbb{C}) := \left\{ \varphi \in C^{\infty}(\mathbb{R}^d, \mathbb{C}) \mid \ \varphi = 0 \text{ outside some bounded set} \right\},$$

but $C_{\mathrm{c}}^{\infty}(\mathbb{R}^d, \mathbb{C})$, endowed with the inner product $\langle \varphi | \psi \rangle$, is not a Hilbert space.

- **To obtain a Hilbert space, we have to "complete" it with "all the limits of the Cauchy sequences of elements of $C_{\mathrm{c}}^{\infty}(\mathbb{R}^d)$". We thus obtain the set**

$$L^2(\mathbb{R}^d, \mathbb{C}) := \left\{ \varphi : \mathbb{R}^d \to \mathbb{C} \mid \int_{\mathbb{R}^d} |\varphi|^2 < \infty \right\},$$

which, endowed with the inner product $\langle \varphi | \psi \rangle$, is a Hilbert space.

- **Technical details:**
  - **one must use the Lebesgue integral (doesn't work with Riemann integral);**
  - **the elements of $L^2(\mathbb{R}^d, \mathbb{C})$ are in fact equivalence classes of measurable functions (for the Lebesgue measure) for the equivalence relation $\varphi \sim \varphi'$ iff $\varphi = \varphi'$ everywhere except possibly on a set of zero Lebesgue measure.**

Fundamental examples: the Sobolev spaces $H^1(\mathbb{R}^d,\mathbb{C})$ and $H^2(\mathbb{R}^d,\mathbb{C})$.

- **The sets**

$$H^1(\mathbb{R}^d,\mathbb{C}) := \left\{\varphi \in L^2(\mathbb{R}^d,\mathbb{C}) \mid \nabla\varphi \in (L^2(\mathbb{R}^d,\mathbb{C}))^d\right\},$$
$$H^2(\mathbb{R}^d,\mathbb{C}) := \left\{\varphi \in L^2(\mathbb{R}^d,\mathbb{C}) \mid \nabla\varphi \in (L^2(\mathbb{R}^d,\mathbb{C}))^d \text{ and } D^2\varphi \in (L^2(\mathbb{R}^d,\mathbb{C}))^{d\times d}\right\}$$

are vector spaces. Respectively endowed with the inner products

$$\langle\varphi|\psi\rangle_{H^1} := \int_{\mathbb{R}^d} \overline{\varphi}\psi + \int_{\mathbb{R}^d} \overline{\nabla\varphi}\cdot\nabla\psi,$$
$$\langle\varphi|\psi\rangle_{H^2} := \int_{\mathbb{R}^d} \overline{\varphi}\psi + \int_{\mathbb{R}^d} \overline{\nabla\varphi}\cdot\nabla\psi + \int_{\mathbb{R}^d} \overline{D^2\varphi} : D^2\psi,$$

they are Hilbert spaces.

- **Technical detail: the gradient and the second derivatives are defined by means of distribution theory.**

Remark. Let $\varphi \in H^1(\mathbb{R}^d)$. A function $\widetilde{\varphi} \in H^1(\mathbb{R}^d)$ can be a very accurate approximation of φ in $L^2(\mathbb{R}^d)$ and a terrible approximation of φ in $H^1(\mathbb{R}^d)$.

For instance, let $\varphi(x) = \frac{1}{1+x^2}$ and $\varphi_n(x) = \left(1 + \frac{\sin(n^2x^2)}{n}\right)\varphi(x)$. The sequence $(\varphi_n)_{n\in\mathbb{N}^*}$ converges to φ in $L^2(\mathbb{R})$ and goes to infinity in $H^1(\mathbb{R})$.

Bounded linear operators on Hilbert spaces

Definition-Theorem (bounded linear operator). A bounded operator on $\mathcal{H}$ is a linear map $\hat{A} : \mathcal{H} \to \mathcal{H}$ such that

$$\|\hat{A}\| := \sup_{\Psi \in \mathcal{H} \setminus \{0\}} \frac{\|\hat{A}\Psi\|}{\|\Psi\|} < \infty.$$

The set $\mathcal{B}(\mathcal{H})$ of the bounded operators on $\mathcal{H}$ is a non-commutative algebra and $\|\cdot\|$ is a norm on $\mathcal{B}(\mathcal{H})$.

Remark. A bounded linear operator A is uniquely defined by the values of the sesquilinear form $\mathcal{H} \times \mathcal{H} \ni (\Psi_1, \Psi_2) \mapsto \langle \Psi_1 | \hat{A}\Psi_2 \rangle \in \mathbb{C}$.

Definition-Theorem (adjoint of a bounded linear operator). Let $A \in \mathcal{B}(\mathcal{H})$. The operator $\hat{A}^\dagger \in \mathcal{B}(\mathcal{H})$ defined by

$$\forall (u, v) \in \mathcal{H} \times \mathcal{H}, \quad \langle u | \hat{A}^\dagger v \rangle = \langle Au | v \rangle,$$

is called the adjoint of A. The operator A is called self-adjoint if $\hat{A}^\dagger = A$.

Endowed with its norm $\|\cdot\|$ and the $*$ operation, $\mathcal{B}(\mathcal{H})$ is a C*-algebra.

(Non necessarily bounded) linear operators on Hilbert spaces

Definition (linear operator). A linear operator on $\mathcal{H}$ is a linear map $\hat{A} : D(\hat{A}) \to \mathcal{H}$, where $D(\hat{A})$ is a subspace of $\mathcal{H}$ called the domain of $\hat{A}$. Note that bounded linear operators are particular linear operators.

Definition (extensions of operators). Let $\hat{A}_1$ and $\hat{A}_2$ be operators on $\mathcal{H}$. $\hat{A}_2$ is called an extension of $\hat{A}_1$ if $D(\hat{A}_1) \subset D(\hat{A}_2)$ and if $\forall u \in D(\hat{A}_1)$, $\hat{A}_2 u = \hat{A}_1 u$.

Definition (unbounded linear operator). An operator $\hat{A}$ on $\mathcal{H}$ which does not possess a bounded extension is called an unbounded operator on $\mathcal{H}$.

Definition (symmetric operator). A linear operator $\hat{A}$ on $\mathcal{H}$ with dense domain $D(\hat{A})$ is called symmetric if

$$\forall \Psi_1, \Psi_2 \in D(\hat{A}) \times D(\hat{A}), \quad \langle \Psi_1 | \hat{A} \Psi_2 \rangle = \langle \hat{A} \Psi_1 | \Psi_2 \rangle.$$

Symmetric operators are not very interesting. Only self-adjoint operators represent physical observables and have nice mathematical properties:

- **real spectrum;**
- **spectral decomposition and functional calculus.**

Definition (adjoint of a linear operator with dense domain). Let A be a linear operator on $\mathcal{H}$ with dense domain $D(\hat{A})$, and $D(\hat{A}^\dagger)$ the vector space defined as

$$D(\hat{A}^\dagger) = \left\{ v \in \mathcal{H} \mid \exists w_v \in \mathcal{H} \text{ s.t. } \forall u \in D(\hat{A}),\ \langle Au|v\rangle = \langle u|w_v\rangle \right\}.$$

The linear operator $\hat{A}^\dagger$ on $\mathcal{H}$, with domain $D(\hat{A}^\dagger)$, defined by

$$\forall v \in D(\hat{A}^\dagger), \quad \hat{A}^\dagger v = w_v,$$

(if w_v exists, it is unique since $D(\hat{A})$ is dense) is called the adjoint of A.

This definition agrees with the previous one for bounded operators.

Definition (self-adjoint operator). A linear operator $\hat{A}$ with dense domain is called self-adjoint if $\hat{A}^\dagger = \hat{A}$ (that is if $\hat{A}$ symmetric and $D(\hat{A}^\dagger) = D(\hat{A})$).

Case of bounded operators:

symmetric $\Leftrightarrow$ self-adjoint.

Case of unbounded operators:

symmetric (easy to check) $\begin{matrix} \Rightarrow \\ \Leftarrow \end{matrix}$ **self-adjoint (sometimes difficult to check)**

Some unbounded self-adjoint operators arising in quantum mechanics

- **position operator along the j axis:**
  - $\mathcal{H} = L^2(\mathbb{R}^d)$,
  - $D(\widehat{r}_j) = \left\{u \in L^2(\mathbb{R}^d) \mid r_j u \in L^2(\mathbb{R}^d)\right\}$, $(\widehat{r}_j\phi)(\mathbf{r}) = r_j\phi(\mathbf{r})$;
- **momentum operator along the j axis:**
  - $\mathcal{H} = L^2(\mathbb{R}^d)$,
  - $D(\widehat{p}_j) = \left\{u \in L^2(\mathbb{R}^d) \mid \partial_{r_j} u \in L^2(\mathbb{R}^d)\right\}$, $(\widehat{p}_j\phi)(\mathbf{r}) = -i\partial_{r_j}\phi(\mathbf{r})$;
- **kinetic energy operator:**
  - $\mathcal{H} = L^2(\mathbb{R}^d)$,
  - $D(T) = H^2(\mathbb{R}^d) := \left\{u \in L^2(\mathbb{R}^d) \mid \Delta u \in L^2(\mathbb{R}^d)\right\}$, $T = -\frac{1}{2}\nabla^2 = -\frac{1}{2}\Delta$;
- **Schrödinger operators in 3D: let $V \in L^2_{\text{unif}}(\mathbb{R}^3, \mathbb{R})$ ($V(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|}$ OK)**
  - $\mathcal{H} = L^2(\mathbb{R}^3)$,
  - $D(H) = H^2(\mathbb{R}^3)$, $H = -\frac{1}{2}\Delta + V$.

Definition-Theorem (spectrum of a linear operator). Let A be a closed[1] linear operator on $\mathcal{H}$.

- **The open set $\rho(A) = \left\{ z \in \mathbb{C} \mid (z - A) \,:\, D(\hat{A}) \to \mathcal{H} \text{ invertible} \right\}$ is called the resolvent set of A. The analytic function**

$$\rho(A) \ni z \mapsto R_z(A) := (z - A)^{-1} \in \mathcal{B}(\mathcal{H})$$

is called the resolvent of A. It holds $R_z(A) - R_{z'}(A) = (z' - z) R_z(A) R_{z'}(A)$.

- **The closed set $\sigma(A) = \mathbb{C} \setminus \rho(A)$ is called the spectrum of A.**

- **If A is self-adjoint, then $\sigma(A) \subset \mathbb{R}$ and it holds $\sigma(A) = \sigma_{\rm p}(A) \cup \sigma_{\rm c}(A)$, where $\sigma_{\rm p}(A)$ and $\sigma_{\rm c}(A)$ are respectively the point spectrum and the continuous spectrum of A defined as**

$$\sigma_{\rm p}(A) \;=\; \left\{ z \in \mathbb{C} \mid (z - A) \,:\, D(\hat{A}) \to \mathcal{H} \text{ non-injective} \right\} = \{\text{eigenvalues of } A\}$$

$$\sigma_{\rm c}(A) \;=\; \overline{\left\{ z \in \mathbb{C} \mid (z - A) \,:\, D(\hat{A}) \to \mathcal{H} \text{ injective but non surjective} \right\}}.$$

[1] **The operator A is called closed if its graph $\Gamma(A) := \left\{ (u, Au),\, u \in D(\hat{A}) \right\}$ is a closed subspace of $\mathcal{H} \times \mathcal{H}$.**

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 $L^2(\mathbb{R}^d)$ with no singular continuous spectrum. [Ex.: the Hamiltonian of the hydrogen atom.]

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 $B_R = \{\mathbf{r} \in \mathbb{R}^d \mid |\mathbf{r}| < R\}$.

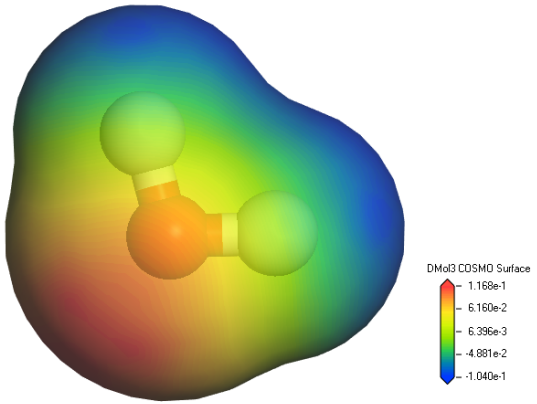
Then

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

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

$\mathcal{H}_{\rm p}$: **subspace of localized states,** $\mathcal{H}_{\rm c}$: **subspace of scattering states**

Electronic problem for a given nuclear configuration $\{\mathbf{R}_A\}_{1\le A\le M}$



Ex: water molecule H_2O

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

$$v_{\mathrm{nuc}}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

$$\left(-\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\mathrm{nuc}}(\mathbf{r}_i) + \sum_{1\le i<j\le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N) = E\, \Psi(\mathbf{x}_1, \cdots, \mathbf{x}_N)$$

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

$$\Psi \in \mathcal{H}_N = \bigwedge^N \mathcal{H}_1, \qquad \mathcal{H}_1 = L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\}; \mathbb{C})$$

Theorem (Kato '51). The operator $\hat{H}_N := -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{1\le i<j\le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

with domain $D(\hat{H}_N) := \mathcal{H}_N \cap H^2((\mathbb{R}^3 \times \{\uparrow, \downarrow\})^N; \mathbb{C})$ **is self-adjoint on** $\mathcal{H}_N$**.**

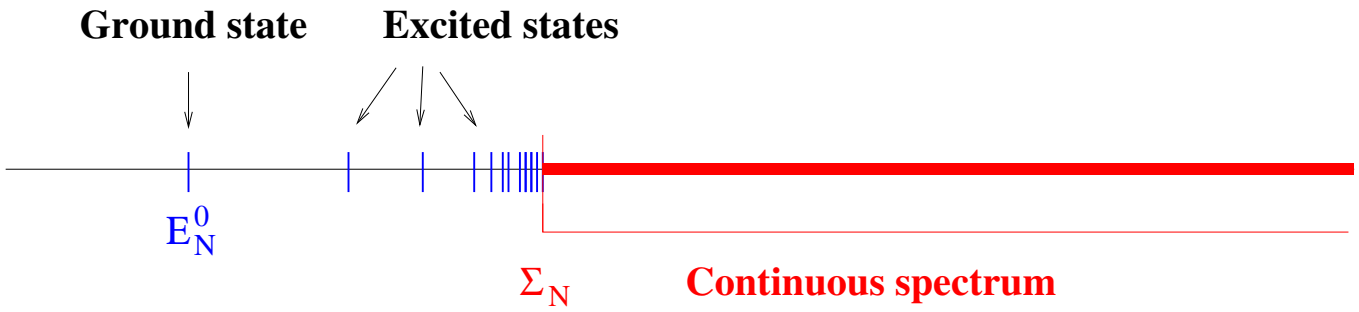
Theorem (spectrum of $\hat{H}_N$).

1. HVZ theorem (Hunziger '66, van Winten '60, Zhislin '60)

$\sigma_{\rm c}(\hat{H}_N) = [\Sigma_N, +\infty)$ **with** $\Sigma_N = \min \sigma(\hat{H}_{N-1}) \leq 0$ **and** $\Sigma_N < 0$ **iff** $N \geq 2$.

2. Bound states of neutral molecules and positive ions (Zhislin '61)

If $N \leq Z := \sum_{A=1}^{M} z_A$**, then** $\hat{H}_N$ **has an infinite number of bound states.**



3. Bound states of negative ions (Yafaev '72)

If $N \geq Z + 1$**, then** $\hat{H}_N$ **has at most a finite number of bound states.**

Spectra of Schrödinger operators with confining potentials

$$\mathcal{H} = L^2(\mathbb{R}^d), \qquad V \in C^0(\mathbb{R}^d), \qquad \lim_{|\mathbf{r}|\to+\infty} V(\mathbf{r}) = +\infty \textbf{ (confining potential)}$$

$$D(\hat{H}) = \left\{ \varphi \in L^2(\mathbb{R}^d) \mid -\frac{1}{2}\Delta\varphi + V\varphi \in L^2(\mathbb{R}^d) \right\}, \quad \forall \varphi \in D(\hat{H}),\ \hat{H}\varphi = -\frac{1}{2}\Delta\varphi + V\varphi.$$

$\hat{H}$ is bounded below and its spectrum is purely discrete ($\sigma_{\mathrm{d}}(\hat{H}) = \sigma(\hat{H})$, $\sigma_{\mathrm{ess}}(\hat{H}) = \emptyset$).

As a consequence, H is diagonalizable in a orthonormal basis: there exist

- **a non-decreasing sequence $(E_n)_{n\in\mathbb{N}}$ of real numbers going to $+\infty$;**
- **an orthonormal basis $(\psi_n)_{n\in\mathbb{N}}$ of $\mathcal{H}$ composed of vectors of $D(H)$,**

such that

$$\forall n \in \mathbb{N}, \quad \hat{H}\psi_n = E_n\psi_n.$$

In addition, the ground state eigenvalue E_0 is non-degenerate and the corresponding eigenvector can be chosen positive on $\mathbb{R}^d$.

Spectra of 3D Schrödinger operators with potentials decaying at infinity

V **such that** $\forall \varepsilon > 0,\ \exists (V_2, V_\infty) \in L^2(\mathbb{R}^3) \times L^\infty(\mathbb{R}^3)$ **s.t.** $V = V_2 + V_\infty$ **and** $\|V_\infty\|_{L^\infty} \leq \varepsilon$,

$$\mathcal{H} = L^2(\mathbb{R}^3), \qquad D(\hat{h}) = H^2(\mathbb{R}^3), \qquad \forall \varphi \in D(\hat{h}),\ \hat{h}\varphi = -\frac{1}{2}\Delta\varphi + V\varphi.$$

The operator H is self-adjoint, bounded below, and $\sigma_{\rm c}(\hat{h}) = [0, +\infty)$.

Depending on V, the discrete spectrum of $\hat{h}$ may be

- **the empty set;**
- **a finite number of negative eigenvalues;**
- **a countable infinite number of negative eigenvalues accumulating at 0 (ex: Ridberg states).**

If $\hat{h}$ has a ground state, then its energy is a non-degenerate eigenvalue and the corresponding eigenvector can be chosen positive on $\mathbb{R}^d$.

The special case of Kohn-Sham LDA Hamiltonians

$$\hat{h}_\rho^{\mathrm{KS}} = -\frac{1}{2}\Delta + V_\rho^{\mathrm{KS}} \quad \textbf{with} \quad V_\rho^{\mathrm{KS}}(\mathbf{r}) = -\sum_{A=1}^{M} \frac{z_A}{|\mathbf{r}-\mathbf{R}_A|} + \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{de_{\mathrm{xc}}^{\mathrm{LDA}}}{d\rho}(\rho(\mathbf{r}))$$

For any $\rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, the KS potential V_ρ^{KS} satisfies the assumptions of the previous slide. In particular H_ρ is bounded below and $\sigma_{\mathrm{c}}(\hat{h}_\rho) = [0, +\infty)$.

Let $Z = \sum_{A=1}^{M} z_A$ be the total nuclear charge of the molecular system and $N = \int_{\mathbb{R}^3} \rho$.

- **If $N < Z$ (positive ion), $\hat{h}_\rho^{\mathrm{KS}}$ has a countable infinite number of negative eigenvalues accumulating at 0.**
- **If $N = Z$ (neutral molecular system) and if ρ_{GS} is a ground state density of the system, then $\hat{h}_{\rho_{\mathrm{GS}}}^{\mathrm{KS}}$ has at least N non-positive eigenvalues.**

Spectra of (restricted) Hartree-Fock Hamiltonians

Let $\Phi = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N$ **be such that** $\displaystyle\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}$**,**

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \phi_i(\mathbf{r}) \phi_i(\mathbf{r}'), \qquad \rho_\gamma(\mathbf{r}) = 2\gamma(\mathbf{r}, \mathbf{r}) = 2 \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2.$$

$$\mathcal{H} = L^2(\mathbb{R}^3), \quad D(H) = H^2(\mathbb{R}^3),$$

$$(\hat{h}_\gamma^{\mathrm{HF}} \phi)(\mathbf{r}) = -\frac{1}{2}\Delta\phi(\mathbf{r}) - \sum_{A=1}^{M} \frac{z_A}{|\mathbf{r} - \mathbf{R}_A|} \phi(\mathbf{r}) + \left(\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \right) \phi(\mathbf{r}) - \int_{\mathbb{R}^3} \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \phi(\mathbf{r}') \, d\mathbf{r}'$$

Let $Z := \sum_{A=1}^{M} z_A$**. The operator** $\hat{h}_\gamma^{\mathrm{HF}}$ **is self-adjoint, bounded below, and we have:**

- $\sigma_{\mathrm{c}} = [0, +\infty)$**;**
- **if** $N < Z$ **(positive ion),** $\hat{h}_\gamma^{\mathrm{HF}}$ **has a countable infinite number of negative eigenvalues accumulating at** 0**;**
- **if** $N = Z$ **(neutral molecular system) and if** Φ_{GS} **is a HF ground state, then** $\hat{h}_{\gamma_{\mathrm{GS}}}^{\mathrm{HF}}$ **has at least** N **negative eigenvalues (counting multiplicities).**

Spectra of Dirac Hamiltonians

$$\mathcal{H} = L^2(\mathbb{R}^3;\mathbb{C}^4), \qquad D(\hat{D}_0) = H^1(\mathbb{R}^3;\mathbb{C}^4), \qquad \hat{D}_0 = c\hat{\vec{p}}\cdot\vec{\alpha} + mc^2\beta$$

$$\hat{p}_j = -\mathrm{i}\hbar\partial_j, \qquad \alpha_j = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \in \mathbb{C}^{4\times 4}, \qquad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix} \in \mathbb{C}^{4\times 4}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \textbf{(Pauli matrices)}$$

The free Dirac operator $\hat{D}_0$ is self-adjoint and

$$\sigma(\hat{D}_0) = \sigma_{\mathrm{c}}(\hat{D}_0) = (-\infty, -mc^2] \cup [mc^2, +\infty).$$

Theorem. **Let** $\alpha := \frac{e^2}{4\pi\varepsilon_0\hbar c} \simeq 1/137.036$ **be the fine structure constant. Let**

$$\hat{D}_Z = \hat{D}_0 - \frac{Z}{|\mathbf{r}|}, \qquad Z \in \mathbb{R} \quad \textbf{(physical cases: } Z = 1, 2, 3, \cdots\textbf{)}.$$

- **if** $|Z| < \frac{\sqrt{3}}{2\alpha} \simeq 118.677$**, the Dirac operator** $\hat{D}_Z$ **is essentially self-adjoint (meaning that there exists a unique domain** $D(\hat{D}_Z)$ **containing** $C_c^\infty(\mathbb{R}^3; \mathbb{C}^4)$ **for which** $\hat{D}_Z$ **is self-adjoint);**
- **if** $|Z| > \frac{\sqrt{3}}{2\alpha} \simeq 118.677$**,** $\hat{D}_Z$ **has many self-adjoint extensions;**
- **if** $|Z| < \frac{1}{\alpha} \simeq 137.036$**,** $\hat{D}_Z$ **has a special self-adjoint extension, considered as the physical one. The essential spectrum of this self-adjoint extension is** $(-\infty, -mc^2] \cup [mc^2, +\infty)$ **and its discrete spectrum consist of the eigenvalues**

$$E_{nj} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - Z^2\alpha^2}} \right)^2 \right]^{-1/2}, \quad n \in \mathbb{N}^*,\ j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots \leq n - \frac{1}{2}.$$

Many-body Dirac-Coulomb Hamiltonian are not understood mathematically.

Functional calculus for diagonalizable self-adjoint operators

Let $\hat{A}$ be a self-adjoint operator that can be diagonalized in an orthonormal basis $(\varphi_n)_{n\in\mathbb{N}}$ (this is not the case for many useful self-adjoint operators!).

Dirac's bra-ket notation: $\hat{A} = \sum_{n\in\mathbb{N}} \lambda_n |\varphi_n\rangle\langle\varphi_n|, \quad \lambda_n \in \mathbb{R}, \quad \langle\varphi_m|\varphi_n\rangle = \delta_{mn}.$

Then,

- **the operator $\hat{A}$ is bounded if and only if $\|\hat{A}\| = \sup_n |\lambda_n| < \infty$;**
- $D(\hat{A}) = \left\{|\psi\rangle = \sum_{n\in\mathbb{N}} c_n|\varphi_n\rangle \mid \sum_{n\in\mathbb{N}}(1+|\lambda_n|^2)|c_n|^2 < \infty\right\}$**;**
- $\sigma_{\mathrm{p}}(\hat{A}) = \{\lambda_n\}_{n\in\mathbb{N}}$ **and** $\sigma_{\mathrm{c}}(\hat{A}) =$ **accumulation points of** $\{\lambda_n\}_{n\in\mathbb{N}} \backslash \sigma_{\mathrm{p}}(\hat{A})$**;**
- $\mathcal{H}_{\mathrm{p}} = \mathcal{H}$ **and** $\mathcal{H}_{\mathrm{c}} = \{0\}$ **(if $\hat{A}$ is a Hamiltonian: no scattering states!);**
- **functional calculus for diagonalizable self-adjoint operators: for all $f : \mathbb{R} \to \mathbb{C}$, the operator $f(\hat{A})$ defined by**

$$D(f(\hat{A})) = \left\{ |\psi\rangle = \sum_{n\in\mathbb{N}} c_n|\varphi_n\rangle \mid \sum_{n\in\mathbb{N}}(1+|f(\lambda_n)|^2)|c_n|^2 < \infty \right\}, \quad f(\hat{A}) = \sum_{n\in\mathbb{N}} f(\lambda_n)|\varphi_n\rangle\langle\varphi_n|$$

is independent of the choice of the spectral decomposition of $\hat{A}$.

Theorem (functional calculus for bounded functions). Let $\mathfrak{B}(\mathbb{R},\mathbb{C})$ be the $*$-algebra of bounded $\mathbb{C}$-valued Borel functions on $\mathbb{R}$ and let $\hat{A}$ be any self-adjoint operator on $\mathcal{H}$. Then there exists a unique map

$$\Phi_A \,:\, \mathfrak{B}(\mathbb{R},\mathbb{C}) \ni f \mapsto f(\hat{A}) \in \mathcal{B}(\mathcal{H})$$

satisfies the following properties:

1. Φ_A is a homomorphism of $*$-algebras:

$$(\alpha f+\beta g)(\hat{A}) = \alpha f(\hat{A})+\beta g(\hat{A}), \quad (fg)(\hat{A}) = f(\hat{A})g(\hat{A}), \quad f^*(\hat{A}) = f(\hat{A})^\dagger;$$

2. $\|f(\hat{A})\| \leq \sup_{x\in\mathbb{R}} |f(x)|$**;**

3. if $f_n(x) \to x$ pointwise and $|f_n(x)| \leq |x|$ for all n and all $x \in \mathbb{R}$, then

$$\forall \psi \in D(\hat{A}), \quad f_n(\hat{A})\psi \to \hat{A}\psi \text{ in } \mathcal{H};$$

4. if $f_n(x) \to f(x)$ pointwise and $\sup_n \sup_{x\in\mathbb{R}} |f_n(x)| < \infty$, then

$$\forall \psi \in \mathcal{H}, \quad f_n(\hat{A})\psi \to f(\hat{A})\psi \text{ in } \mathcal{H};$$

In addition, if $\psi \in \mathcal{H}$ is such that $\hat{A}\psi = \lambda\psi$, then $f(\hat{A})\psi = f(\lambda)\psi$.

Theorem (spectral projections and functional calculus - general case -).

Let $\hat{A}$ be a self-adjoint operator on $\mathcal{H}$.

- **For all $\lambda \in \mathbb{R}$, the bounded operator $\hat{P}^A_\lambda := \mathbb{1}_{(-\infty,\lambda]}(\hat{A})$, where $\mathbb{1}_{(-\infty,\lambda]}(\cdot)$ is the characteristic function of $(-\infty, \lambda]$, is an orthogonal projection.**

- **Spectral decomposition of $\hat{A}$: for all $\psi \in D(\hat{A})$ and $\psi' \in \mathcal{H}$, it holds**

$$\langle \psi' | \hat{A}\psi \rangle = \int_{\mathbb{R}} \lambda \underbrace{d\langle \psi' | \hat{P}^A_\lambda \psi \rangle}_{\text{Bounded complex measure on } \mathbb{R}}, \quad \textbf{which we denote by} \quad \hat{A} = \int_{\mathbb{R}} \lambda \, d\hat{P}^A_\lambda.$$

- **Functional calculus: let f be a (not necessarily bounded) $\mathbb{C}$-valued Borel function on $\mathbb{R}$. The operator $f(A)$ can be defined by**

$$D(f(\hat{A})) := \left\{ \psi \in \mathcal{H} \mid \int_{\mathbb{R}} |f(\lambda)|^2 \underbrace{d\langle \psi | P^A_\lambda \psi \rangle}_{\text{Bounded positive measure on } \mathbb{R}} < \infty \right\}$$

and

$$\forall (\psi, \psi') \in D(f(\hat{A})) \times \mathcal{H}, \ \langle \psi' | f(\hat{A})\psi \rangle := \int_{\mathbb{R}} f(\lambda) \, d\langle \psi' | \hat{P}^A_\lambda \psi \rangle.$$

Application of spectral theory and functional calculus: one-body density matrices

1-RDM associated with an N-body wavefunction Ψ_N

$$\gamma_{\Psi_N}(\mathbf{x},\mathbf{x}') := \langle \psi_N | \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}(\mathbf{r}') | \Psi_N \rangle$$
$$= N \int_{(\mathbb{R}^3\times\{\uparrow,\downarrow\})^{N-1}} \Psi_N(\mathbf{x},\mathbf{x}_2,\cdots,\mathbf{x}_N)\Psi_N(\mathbf{x}',\mathbf{x}_2,\cdots,\mathbf{x}_N)^* \, d\mathbf{x}_2\cdots d\mathbf{x}_N$$

It is extremely fruitful to consider $\gamma_{\Psi_N}(\mathbf{x},\mathbf{x}')$ as the integral kernel of an operator $\hat{\gamma}_{\Psi_N}$ on $\mathcal{H}_1$ (also called 1-RDM or DM for short)

$$\forall \varphi \in \mathcal{H}_1, \quad (\hat{\gamma}_{\Psi_N}\varphi)(\mathbf{x}) = \int_{\mathbb{R}^3\times\{\uparrow,\downarrow\}} \gamma_{\Psi_N}(\mathbf{x},\mathbf{x}')\,\varphi(\mathbf{x}')\,d\mathbf{x}'$$

The operator $\hat{\gamma}_{\Psi_N}$ is self-adjoint, diagonalizable, $\sigma(\hat{\gamma}_{\Psi_N}) \subset [0,1]$, and $\mathrm{Tr}(\hat{\gamma}_{\Psi_N}) = N$

$$\hat{\gamma}_{\Psi_N} = \sum_{j=1}^{+\infty} n_j |\varphi_j\rangle\langle\varphi_j|, \quad \langle\varphi_j|\varphi_{j'}\rangle = \delta_{jj'}, \quad 0 \le n_j \le 1, \quad \sum_{j=1}^{+\infty} n_j = N$$

The φ_j's are called the natural orbitals (associated with Ψ_N), and the n_j's the natural occupation numbers

Application of spectral theory and functional calculus: one-body density matrices

When Ψ_N is the Slater determinant of orthonormal orbitals $(\varphi_1, \cdots, \varphi_N)$, then $\hat{\gamma}_{\Psi_N}$ is the orthogonal projector on span$(\varphi_1, \cdots, \varphi_N)$:

$$\hat{\gamma}_{\Psi_N} = \sum_{j=1}^{N} |\varphi_j\rangle\langle\varphi_j|, \qquad \hat{\gamma}_{\Psi_N}^2 = \hat{\gamma}_{\Psi_N} = \hat{\gamma}_{\Psi_N}^\dagger$$

Application of spectral theory and functional calculus: one-body density matrices

Consider a system of non-interacting "electrons" with one-body Hamiltonian $\hat{h}$

Assume that $\hat{h}$ has at least N eigenvalues $\varepsilon_1 \leq \varepsilon_2 \leq \cdots \leq \varepsilon_N$ (counting multiplicities) and that $\varepsilon_N < \varepsilon_{N+1}$ (energy gap). Then

- **NVE ground-state density matrix is**

$$\hat{\gamma}_{\mathrm{NVE}} = \mathbb{1}_{(-\infty,\mu_{\mathrm{F}}]}(\hat{h})$$

  where μ_{F} is any number in the range $[\varepsilon_N, \varepsilon_{N+1})$ (Fermi level)

Assume that $\hat{h}$ is diagonalizable: $\hat{h} = \sum_{j=1}^{+\infty} \varepsilon_j |\varphi_j\rangle\langle\varphi_j|, \quad \langle\varphi_j|\varphi_{j'}\rangle = \delta_{jj'}$

- **NVT (canonical) ground-state density matrix:**

$$\hat{\gamma}_{\mathrm{NVT}} = f_\beta(\hat{h} - \mu), \quad \mu \text{ such that } \mathrm{Tr}(\hat{\gamma}_{\mathrm{NVT}}) = N, \quad f_\beta(\varepsilon) = \frac{1}{1 + e^{\beta\varepsilon}}$$

- **μVT (grand-canonical) ground-state density matrix:**

$$\hat{\gamma}_{\mu\mathrm{VT}} = f_\beta(\hat{h} - \mu)$$