A Generalized *Aufbau principle* for Linear Partial Differential Operators

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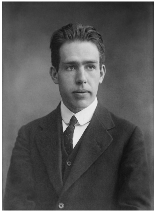
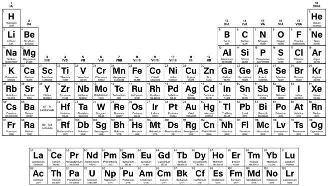


Niels Bohr[1]



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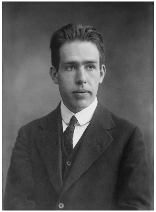

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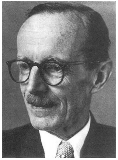
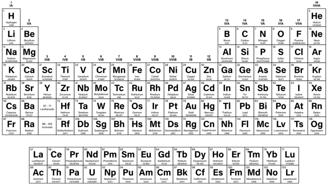


Erwin Madelung[3]



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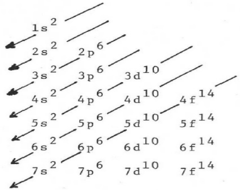

Figure 1. Device for remembering order in which electrons are added to atoms.

Madelung's Rule[4]

[1] https://en.wikipedia.org/wiki/File:Niels_Bohr_-_LOC_-_ggbain_-_35303.jpg.

[2] https://www.philipharris.co.uk/blog/secondary/international-year-of-the-periodic-table/

[3] https://alchetron.com/Erwin-Madelung.

[4] D. Pan Wong, *Theoretical Justification of Madelung's Rule*, J. Chem. Ed. Vol. 56, 11, 1979.

Motivation

Problem

Is it possible (or even needed) to formulate a theoretical proof of the Aufbau principle?

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- *E.R. Scerri, V. Kreinovich and P. Wojciechowski in* Ordinal explanation of the periodic system of chemical elements, *Int. J. Uncertainty, Fuzziness and Knowledge-Based Systems Vol. 6, 387-399, 1998.*

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Example

Aufbau principle in *Electronic Structure Theory* calculations with approximated optimization models of the Hamiltonian $\mathbb{H}$:

$$\min_{\Psi \in \mathcal{D}(\mathbb{H})} \mathcal{E}(\mathbb{H}, \Psi) \to \Psi_0 \text{ with } E_0.$$

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- V. Bach, E.H. Lieb, M. Loss and J.P. Solovej, *There are No Unfilled Shells in Unrestricted Hartree–Fock Theory*, Phys. Rev. Lett. Volume 72, 19, 2981-2983, 1994.
- K.J.H. Giesbertz and E.J. Baerends, *Aufbau derived from a unified treatment of occupation numbers in Hartree–Fock, Kohn-Sham, and natural orbital theories with the KKT conditions for the inequality constraints $n_i \leq 1$ and $n_i \geq 0$*, J. Chem. Phy. 132, 194108, 2010.

Tensor products

Tensor products

Definition (Tensor product of operators[1])

Let A and B be linear, not necessarily bounded and densely defined operators on the Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$. The Tensor product between A and B is the closure of $A \otimes B$ on the tensor product of the domains $\mathcal{D}(A) \otimes \mathcal{D}(B)$, which is the well defined operator:

$$\begin{aligned} A \otimes B : \quad D(A) \otimes D(B) &\mapsto \mathcal{H}_1 \otimes \mathcal{H}_2 \\ \phi \otimes \psi &\mapsto (A \otimes B)(\phi \otimes \psi) = A\phi \otimes B\psi \end{aligned}$$

[1] M. Reed and B. Simon, *Methods of Modern Mathematical Physics I*, chapter VIII.10, Academic Press 1972.

Notation

Let $\mathcal{H}$ be a Hilbert space. We denote

$$\mathcal{H}_N := \mathcal{H} \otimes \cdots \otimes \mathcal{H}$$

as the N-dimensional Hilbert space tensor product from $\mathcal{H}$. Further we define H_k as a family of essentially self–adjoint operators on $\mathcal{D}(H_k) \subset \mathcal{H}$ for $k = 1, \ldots, N$.

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as the N-dimensional Hilbert space tensor product from $\mathcal{H}$. Further we define H_k as a family of essentially self–adjoint operators on $\mathcal{D}(H_k) \subset \mathcal{H}$ for $k = 1, \ldots, N$. Since tensor products of Hilbert spaces induce an isomorphism to higher dimensional Hilbert spaces, we will also use the following notation for the family of operators now acting on $\mathcal{H}_N$

$$\tilde{H}_k = \overline{\mathcal{I} \otimes \cdots \otimes \underbrace{H_k}_{k\text{th position}} \otimes \cdots \otimes \mathcal{I}},$$

where $\mathcal{I}$ is the identity operator on $\mathcal{H}$. The $\tilde{H}_k$ are still essentially self–adjoint on the tensor product $\mathcal{H} \otimes \cdots \otimes \underbrace{\mathcal{D}(H_k)}_{k\text{th position}} \otimes \cdots \otimes \mathcal{H}$.

Tensor products

Theorem (Linear combination of tensor products of operators[1])

Consider now $P(x_1, \ldots, x_N)$ as a polynomial with real coefficients of degree n_k in the kth variable. Further let H_k be a family of operators which are essentially self–adjoint on $\mathcal{D}(H_k)$. Then,

- $P(\tilde{H_1}, \ldots, \tilde{H_N})$ *is essentially self–adjoint on*

$$D := \bigotimes_{k_=1}^{N} \mathcal{D}(H_k^{n_k})$$

- $\sigma(\overline{P(\tilde{H_1}, \ldots, \tilde{H_k})}) = \overline{P(\sigma(H_1), \ldots, \sigma(H_N))},$

where $\sigma(H_K)$ stands for the spectrum of the operator H_k. Note that $\mathcal{D}(H_k^{n_k}) \subseteq \mathcal{D}(H_k)\ \forall n_k \in \mathbb{N}$.

[1] *M. Reed and B. Simon,* Methods of Modern Mathematical Physics I, *Theorem VIII.33, Academic Press 1972.*

Spectral Theory

We denote $\sigma_d(H_k)$ as the discrete spectrum of H_k containing all isolated eigenvalues with finite multiplicity. Furthermore for $\lambda \in \sigma_d(H_k)$ let the eigenspace corresponding to the eigenvalue λ be

$$\mathrm{eig}(\lambda) := \{\phi \in \mathcal{H} |\ \phi \in Ker(H_k - \lambda\mathcal{I})\}.$$

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Now the so–called *Min-Max Theorem*[1] provides us an ordering of the eigenvalues in $\sigma_d(H_k)$ with corresponding eigenfunctions in $\mathrm{eig}(\sigma_d(H_k))$. That is

$$\varepsilon_1 \leq \varepsilon_2 \leq \ldots \text{ and } \phi_1, \phi_2, \ldots \text{ from solving } H_k \phi_n = \varepsilon_n \phi_n.$$

Since H_k are essentially self–adjoint, the ordered eigenfunctions yield an orthonormal basis $(\phi_n)_n$ in $\mathcal{D}(H_k)$.

[1] R. Courant, *Über Eigenwerte bei den Differentialgleichungen der mathematischen Physik*, Mathematische Zeitschrift, Band 7, No. 1-4, 1-57, 1920.

Main idea

Definition (A generalized *Aufbau principle*)

Let H be an essentially self–adjoint operator on $\mathcal{D}(H) \subset \mathcal{H}_N$. If $H = P(\tilde{H_1}, \dots, \tilde{H_N})$ with $\dim(\text{eig}(\sigma_d(H_k))) \geq 1$ for $k = 1, \dots, N$, then we denote the span of the N-dimensional tensor product of the orthonormal basis from $\text{eig}(\sigma_d(H_k))$ as

$$B_N := \left\{ \psi \in \mathcal{H}_N | \psi = \sum_{n_1,\dots,n_N} \alpha_{n_1 \dots n_N} (\phi_{n_1} \otimes \cdots \otimes \phi_{n_N}), \sum_{|n|=1} |\alpha_{n_1 \dots n_n}|^2 = 1 \right\},$$

where the sum goes over all multi–indicies $n_1, \dots, n_N$.

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where the sum goes over all multi–indicies $n_1, \dots, n_N$. We say now H satisfies the general *Aufbau principle*, i.e.

$$\arg\min_{\psi \in B_N} \langle \psi \,|\, H\psi \rangle_{\mathcal{H}_N} = \alpha_{1\dots1}(\phi_1 \otimes \cdots \otimes \phi_1).$$

Hence in order to obtain the N-dimensional grorund state one uses the minimizing eigenfunctions from the single dimensional operator.

Examples

Examples

Example (Ritz's method[1])

We start with a (essentially) self–adjoint operator H on the N-dimensional Hilbert space $\mathcal{H}_N$. The goal is to minimize the corresponding energy functional, i.e. find the lower bound of the spectrum

$$\min_{\substack{\psi\in\mathcal{D}(H)\\ \|\psi\|=1}} \langle \psi \,|\, H\psi \rangle \,.$$

Ritz's idea was to perform an optimization of parameters which correspond to a test function $\psi_a = \sum_m a_m \varphi_m$, where the $(\varphi_m)_m$ is a suitable chosen basis set. Thus

$$\min_{\substack{\psi\in\mathcal{D}(H)\\ \|\psi\|=1}} \langle \psi \,|\, H\psi \rangle \leq \min_{a_m} \langle \psi_a \,|\, H\psi_a \rangle \,.$$

[1] M.J. Gander and G. Wanner, *From Euler, Ritz, and Galerkin to Modern Computing*, SIAM Review Vol. 54, No. 4, 2012.

Examples

Example (Ritz's method)

If now H satisfies our *Aufbau principle*, then one can choose the $(\varphi_m)_m$ to be in the span of the N-dimensional tensor product of the orthonormal basis B_N:

$$\varphi_m = \sum_{n_1,\dots,n_N}^{m} \alpha_{n_1\dots n_N}(\phi_{n_1} \otimes \cdots \otimes \phi_{n_N}) \text{ with } \sum_{|n|=1}^{m} |\alpha_{n_1\dots n_N}|^2 = 1.$$

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Finally the first basis function, which yields the smallest eigenvalue of H on B_N will be chosen as the tensor product of the minimizers from the discrete spectrum of H_k. That is

$$\varphi_1 = \alpha_{1\dots 1}(\phi_1 \otimes \cdots \otimes \phi_1).$$

Examples

Example (Application of Ritz's method)

Let us consider an easy example. We are going to construct the two–dimensional vibration eigenfunctions by using the single–dimensional ones. Thus we have a compact set $\Omega \times \Omega = \Omega^2 \subset \mathbb{R}^2$ and $H := -\Delta$ acting on $\mathcal{H}_2 := L^2(\Omega^2)$. Then we can define

$$\tilde{H}_1 := \overline{-\Delta_1 \otimes \mathcal{I}} \text{ and } \tilde{H}_2 := \overline{\mathcal{I} \otimes -\Delta_2},$$

such that $H = \tilde{H}_1 + \tilde{H}_2$ is on $D := C_c^\infty(\Omega) \otimes C_c^\infty(\Omega)$ essentially self–adjoint[1]. So we can find the one–dimensional eigenspace by solving

$$\begin{cases} -\Delta\phi = \varepsilon\phi & \text{in } \Omega \\ \phi = 0 & \text{on } \partial\Omega. \end{cases}$$

[1] M. Loss, http://people.math.gatech.edu/ loss/14SPRINGTEA/laplacian.pdf, accessed 28.06.2019.

Example (Application of Ritz's method)

The solution yields indeed a discrete ordered spectrum $\varepsilon_1 \leq \varepsilon_2 \leq \ldots$ and corresponding eigenfunctions $\phi_1, \phi_2, \ldots$. Finally we can use the Theorem for *Linear combination of tensor products of operators* in order to find the lowest eigenvalue of the two–dimensional operator.
$P(\tilde{H_1}, \tilde{H_2}) := \tilde{H_1} + \tilde{H_2} = H$

$$\Rightarrow \min \sigma_d(H) = \min P(\sigma_d(H_1), \sigma_d(H_2)) = \min \sigma_d(H_1) + \min \sigma_d(H_2).$$

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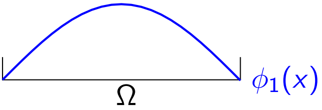
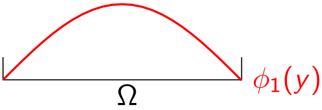
Hence the corresponding minimizer from H will be just the direct (tensor) product of the minimizer from H_1 and H_2. That is

$$\begin{aligned} \psi_{11}(x,y) := \underset{\psi \in D}{\arg\min} \langle \psi \,|\, H\psi \rangle &= \underset{\phi \in C_c^\infty(\Omega)}{\arg\min} \ \langle \phi \,|\, H_1 \phi \rangle \otimes \underset{\phi \in C_c^\infty(\Omega)}{\arg\min} \ \langle \phi \,|\, H_2 \phi \rangle \\ &= \phi_1(x)\phi_1(y). \end{aligned}$$

Examples





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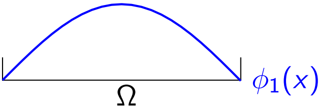

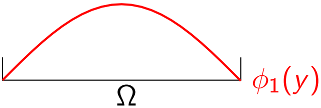

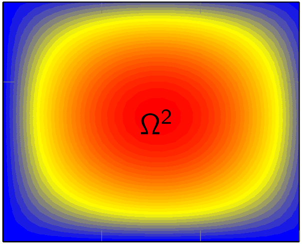

$\psi_{11}(x, y)$

Examples

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Example (Non–interacting Quantum systems[1])

The many–particle unrestricted electronic Hamiltonian for N non–interacting electrons is

$$\mathbb{H} := \sum_{k=1}^{N} \left[-\Delta_k + V(x_k) \right].$$

The corresponding quantum system is fully described by solving the so–called *Schrödinger equation* $\mathbb{H}\Psi = E\Psi$. Equivalently one computes the stationary states of the energy functional, i.e. the inner product of $\mathbb{H}$ and a normalized function Ψ in the Hilbert space $\mathcal{H}_N := L^2(\mathbb{R}^{3N})$

$$\min_{\Psi \in \mathcal{D}(\mathbb{H})} \mathcal{E}(\mathbb{H}, \Psi) = \min_{\Psi \in \mathcal{D}(\mathbb{H})} \langle \Psi \,|\, \mathbb{H}\Psi \rangle = E > -\infty.$$

Thus we can apply the same technique as for the *Ritz's method*!

[1] A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*, Dover Publications, 2015.

Example (Non–interacting Quantum systems)

The N-dimensional Hilbert space $\mathcal{H}_N$ is isomorphic[1] to the N-dimensional tensor product of the single particle Hilbert spaces

$$L^2(\mathbb{R}^{3N}) \cong L^2(\mathbb{R}^3) \otimes \cdots \otimes L^2(\mathbb{R}^3).$$

Thus consider now the family of operators $H_k := -\Delta_k + V(x_k)$ on $\mathcal{H} = L^2(\mathbb{R}^3)$. The H_k are essentially self–adjoint[2] on $\mathcal{D}(H_k) := C_c^\infty(\mathbb{R}^3)$ under conditions on V. Now we can use our notation for tensor products of operators in order to seperater $\mathbb{H}$

$$\mathbb{H} = \sum_{k=1}^{N} \overline{\mathcal{I} \otimes \cdots \otimes H_k \otimes \cdots \otimes \mathcal{I}}.$$

[1] M. Reed and B. Simon, *Methods of Modern Mathematical Physics I*, Theorem II.10, Academic Press 1972.
[2] M. Reed and B. Simon, *Methods of Modern Mathematical Physics II*, Theorem X.15, Academic Press 1975.

Examples

Example (Non–interacting Quantum systems)

With the Theorem we know that $\mathbb{H}$ is essentially self–adjoint on

$$D := \bigotimes_{k=1}^{N} \mathcal{D}(H_k).$$

Furthermore the discrete spectrum of the single particle operators H_k can be found below the essential spectrum with corresponding ordered eigenstates[1]. We can construct once more the set B_N and minimize the energy functional by using the minimizers from the eigenspace of H_k for the discrete spectrum $\sigma_d(H_k)$. Finally this is corresponds just to the definition of our *Aufbau principle* for the many–particle electronic Hamiltonian for non-interacting electrons!

[1] E.H. Lieb and M. Loss, *ANALYSIS*, 2nd edition, Graduate Studies in Mathematics Vol. 14, American Mathematical Society, 2001.

The Pauli–principle

However one important property of electrons has been neglected so far, the so–called *Pauli–principle*.

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Definition (The Pauli–principle[1])

The total electronic wave function obtained by the *Schrödinger equation* must be antisymmetric under interchange of two coordinates. Consequently two different electrons are not allowed to be in the same single state.

Thus a new concept for our generalized *Aufbau principle* is needed!

[1] A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*, Dover Publications, 2015.

Additional models

Definition (Antisymmetric tensor product Hilbert space[1])

We define first $A_N := \frac{1}{\sqrt{N}} \sum_{\tau \in S_N} \operatorname{sign}(\tau)\tau$ which is an orthogonal projection with S_N as the permutation group on N elements and τ defined as the operator

$$\tau(\phi_{k_1} \otimes \cdots \otimes \phi_{k_N}) = \phi_{k_{\tau(1)}} \otimes \cdots \otimes \phi_{k_{\tau(N)}}$$

for an arbitrarily chosen basis set in $\mathcal{H}_N$. Then the N-dimensional antisymmetric tensor product Hilbert space is denoted as

$$\mathcal{H}_N^A := A_N \mathcal{H}_N.$$

[1] M. Reed and B. Simon, *Methods of Modern Mathematical Physics I*, II.4, Academic Press 1972.

Antisymmetric model

Now our essentially self–adjoint N-dimensional operator H needs to be defined as well on the antisymmetric domain

$$\mathcal{D}^A(H) := A_N D = A_N \bigotimes_{k=1}^{N} \mathcal{D}(H_k).$$

And in the same way we get an antisymmetric span of the N-dimensional tensor product of the orthonormal basis from $\mathrm{eig}(\sigma_d(H_k))$, that is $B_N^A := A_N B_N$

$$= \Big\{ \Psi \in \mathcal{H}_N^A \mid \Psi \;=\; \frac{1}{\sqrt{N}} \sum_{\tau \in S_N} \mathrm{sign}(\tau) \sum_{n_{\tau(1)},\dots,n_{\tau(N)}} \alpha_{n_{\tau(1)}\dots n_{\tau(N)}} (\phi_{n_{\tau(1)}} \otimes \cdots \otimes \phi_{n_{\tau(N)}}), \sum_{|n|=1} |\alpha_{n_{\tau(1)}\dots n_{\tau(N)}}|^2 = 1 \Big\}.$$

Antisymmetric model

Definition (Antisymmetric *Aufbau principle*)

If the N–dimensional operator H on $\mathcal{H}_N^A$ can be represented as $H = P(\tilde{H}_1, \ldots, \tilde{H}_N)$ then we say H satisfies the *antisymmetric Aufbau principle*, i.e.

$$\arg\min_{\Psi \in B_N^A} \langle \Psi \mid H\Psi \rangle = \frac{1}{\sqrt{N}} \sum_{\tau \in S_N} \operatorname{sign}(\tau) \sum_{n_{\tau(1)},\ldots,n_{\tau(N)}=1}^{N} \alpha_{n_{\tau(1)}\ldots n_{\tau(N)}} (\phi_{n_{\tau(1)}} \otimes \cdots \otimes \phi_{n_{\tau(N)}}).$$

The antisymmetric tensor product of the first N different one–dimensional state functions corrersponding to the first N eigenvalues in $\operatorname{eig}(\sigma_d(H_k))$ provide the ground state for the total N-dimensional system.

Quantum chemistry models

Problem (Non–Separability of the full many–particle Hamiltonian)

The full many–particle Hamiltonian for a quantum chemical system is not straight forward separable. That is due to the interaction term in $\mathbb{H}$*;*

$$\mathbb{H} = \sum_{k=1}^{N} \left[-\Delta_k + V(x_k) + \sum_{m=1}^{N} W(x_k, x_m) \right].$$

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Example (Quantum chemical methods[1])

In quantum chemistry one uses different models for the approximation, such as *Hartree–Fock* or *Kohn–Sham Density Functional Theory* which provide respectively different single–particle Hamiltonians H_k with a chosen basis set

$$\min_{\substack{\Psi \in \mathcal{D}(\mathbb{H}) \\ \|\Psi\|=1}} \mathcal{E}(\mathbb{H}, \Psi) \leq \min_{\substack{(\phi_n)_n \subset \mathcal{D}(H_k) \\ \langle \phi_k \mid \phi_m \rangle = \delta_{km}}} \left[\sum_{k=1}^{N} \langle \phi_n \mid H_k \phi_n \rangle + \tilde{W}[\Psi((\phi_n)_n)] \right].$$

[1] A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*, Dover Publications, 2015.

Outlook

Problem (Violation of the *Aufbau principle*)

There are several examples in the literature where a violation of the Aufbau principle is known[1,2] *. The computation results yield some filled obitals with a higher energy then some unfilled ones in the total ground state.*

[1] *A. Makmal, S. Kümmel and L. Kronik*, Dissociation of diatomic molecules and the exact exchange Kohn–Sham potential: The case of LiF, *Phys. Rev. A83, 062512, 2011.*
[2] *E. Scerri*, The trouble with the aufbau principle, *published in Education in Chemistry, 07.11.2013.*

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With a mathematical concept of the *Aufbau principle* we can address the problems by investigating the following properties

- Finite dimensional basis sets for numerical calculations
- Separability of self–adjoint operators[3]
- Extentions of the constrained domains[4]
- ...

[3] S. Huzinaga and A.A Cantu, *Theory of Separability of Many–Electron Systems*, J. Chem. Phys. **55**, 5543 (1971).
[4] C. Li, J. Lu and W. Yang, *On extending Kohn-Sham density functionals to systems with fractional number of electrons*, J. Chem. Phys. **146**, 214109 (2017).

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Thank you for your attention!