A SURVEY FOR THE SPECTRAL PROPERTY OF THE $N-$BODY ELECTRONIC HAMILTONIAN

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Abstract. We review standard results of the literature regarding the spectrum of the $N-$body electronic Hamiltonian $H(N)$ (*i.e* the molecular Hamiltonian under Born-Oppenheimer approximation). As guidance, we shall try to answer the general question *Does $H(N)$ have eigenvalues and if so, where are they located within its spectrum ?* Recalling seminal results and some important techniques to tackle this paramount issue, we contribute (for a modest amount) by extending to the molecular setting the bound of [23] stating the absence of eigenvalues for $H(N)$ when $N \geqslant 4Z+1$ in the atomic case.

Contents

1. Preliminaries

1.1. **Physical aspects.** Given M nuclei $(R_i, Z_i)_{i=1}^M$, where $R_i \in \mathbb{R}^3$ denotes the coordinate of the i-th nucleus and Z_i its nuclear charge, we introduce the *molecular Hamiltonian* $H(N)$ describing N electrons in the electric field generated by the nuclei:

$$H(N) = \sum_{i=1}^{N} -\Delta_{x_i} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|} + \frac{1}{2} \sum_{1 \leqslant i \neq j \leqslant N} \frac{1}{|x_i - x_j|}.$$

Following the *Born-Oppenheimer approximation*, justified by the substantial difference in magnitude between the electronic and nuclear masses, the nuclei

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are treated as classical point-like particles, *i.e.* the R_i's are considered to be fixed. The Hamiltonian $H(N)$ is sometimes referred to as the *electronic* or *clamped-nucleus Hamiltonian*.

Remark 1. Under Born-Oppenheimer approximation, the self-interaction between the nuclei, that is $\frac{1}{2}\sum_{1\leqslant i\neq j\leqslant M}\frac{Z_iZ_j}{|R_i-R_j|}$, is constant and therefore can be ignored for convenience.

Remark 2. Note that the Born-Oppenheimer approximation is similar to demand that the wave function $\psi \in L^2(\mathbb{R}^{3(N+M)})$ representing the entier molecule factors into an electronic and a nuclear component, *i.e.* $\psi \approx \psi_{elec}(x_1,\dots,x_N)\otimes\psi_{nucl}(R_1,\dots,R_M)$ with $\psi_{elec}\in H^2_a(\mathbb{R}^{3N})$. For a general mathematical discussion on the Born-Oppenheimer approximation, we refer the reader to [2, 3, 4, 16, 17, 20, 38].

Whence $H(N)$ is a densely-defined semi-bounded self-adjoint operator over the fermionic $N-$particule space, that is the space of anti-symmetric square-integrable functions $L^2_a(\mathbb{R}^{3N}) := \bigwedge_{i=1}^N L^2(\mathbb{R}^3)$, and its domain[1] of self-adjointness is explicitly given by the anti-symmetric Sobolev space $H^2_a(\mathbb{R}^{3N}) := L^2_a(\mathbb{R}^{3N})\cap H^2(\mathbb{R}^{3N})$ [18, 19, 22, 31]. We recall that electrons are fermionic particules, as they obey the *Pauli exclusion principle*, meaning that any two electrons of a quantum system cannot occupy the same quantum state.

The evolution of the N electrons is given by the famous *Schrödinger equation*, *i.e.*

$$\begin{cases} i\hbar\dfrac{\partial}{\partial t}\Psi(t) = H(N)\Psi(t) \\ \Psi(0) = \Psi_0 \in L^2(\mathbb{R}^{3N}). \end{cases} \tag{1}$$

The solution to the Cauchy problem defined Eq. (1) is uniquely given (at least in a weak sense) by $\Psi(t) = e^{-itH(N)/\hbar}\Psi_0$. A *stationary state* is a particular solution of the form $\Psi(t) = e^{-itE/\hbar}\Psi$, where Ψ is an eigenvector of $H(N)$ associated with the eigenvalue (*i.e.* energy) $E\in\mathbb{R}$, that is $H(N)\Psi = E\Psi$ with $\Psi\in D(H(N))$. Physically, these stationary states represent *observable states*, those states which can, namely, be observed in the concrete world. Therefore, it is not only a whim of mathematicians but an important enquiry for applied chemists and physicists to study and have a good understanding of the spectral properties of $H(N)$.

In what follows, we denote $\Sigma(N) := \min\sigma_{ess}(H(N))$ the *ionization threshold* and $E(N) := \min\sigma(H(N))$ the *ground-state energy*. We recall that $E(N)$ can be obtained through variational methods, for we have

$$E(N) = \inf_{\substack{\psi\in H^2_a(\mathbb{R}^{3N}),\\ \|\psi\|_{L^2(\mathbb{R}^{3N})}=1}} \mathcal{E}(\psi),$$

where $\mathcal{E}(\psi) := \langle H(N)\psi,\psi\rangle$ is the quadratic form associated with $H(N)$, defined over the Sobolev space $H^1_a(\mathbb{R}^{3N}) := L^2_a(\mathbb{R}^{3N})\cap H^1(\mathbb{R}^{3N})$. The (not necessarily unique) eigenvector associated to $E(N)$, if any, is of crucial importance for quantum chemists and physicists, as it represents the state of lowest energy, and therefore the quantum configuration in which one is the most likely to find the N electrons around the M nuclei.

[1]Note that, for simplicity, we have neglected the spins.

1.2. **The HVZ theorem.** As it turns out, $H(N)$ exhibits a spectrum of a rather simple type. This is the object of the so-called HVZ *theorem*, proved by Zhislin [43], Van Winter [41] and Hunziker [14] in the 60's. Note that this theorem is not exclusive to $H(N)$, as it embraces the relatively large class of Schrödinger operators of the form $H = \sum_i -\Delta_{x_i} + \sum_i V(x_i) + \frac{1}{2}\sum_{i\neq j} w(x_i - x_j)$, where the potential V and pairwise interaction w are well-behaved. We recall the theorem in the case of purely repulsive self-interaction, that is $w \geqslant 0$:

Theorem 1 (HVZ theorem)**.** *The essential spectrum $\sigma_{ess}(H(N))$ of the N-body electronic Hamiltonian is given by the half-line*

$$\sigma_{ess}(H(N)) = [\Sigma(N), \infty).$$

Moreover, we have that $\Sigma(N) = E(N-1)$ for all $N \geqslant 1$.

Remark 3. This theorem is fairly intuitive from a physical perspective. Indeed, given N electrons, we can take one electron and *send it at infinity* while the $N-1$ electrons left on sight will occupy the ground-state energy $E(N-1)$ of the subsystem Hamiltonian $H(N-1)$. Besides, because the self-interaction between the electrons is of a repulsive kind, sending more than one electron to infinity will automatically add up energy to the system.

We shall not give a detailed proof of this theorem. Instead, we only give a partial proof of the statement that is reminiscent of the above remark, that is $[E(N-1), \infty) \subset \sigma_{ess}(H(N))$ for all $N \geqslant 1$. It would be left thereafter to prove the converse bound, namely that $\Sigma(N) \geqslant E(N-1)$, which is significantly more complicated. Readers interested in a thorough and complete proof are referred to [21, 22, 32, 39].

Partial proof of Theorem 1. Let us prove that $[E(N-1), \infty) \subset \sigma_{ess}(H(N))$. For simplicity, we ignore the antisymmetry constraint. Let $\psi_{N-1} \in H^2(\mathbb{R}^{3(N-1)})$ be such that $\|\psi_{N-1}\| = 1$ and $\|(H(N-1) - E(N-1))\psi_{N-1}\| \leqslant \varepsilon$, and $\psi_1 \in H^2(\mathbb{R}^3)$ be such that $\|\psi_1\| = 1$ and $\|(-\Delta - \lambda)\psi_1\| \leqslant \varepsilon$ for some $\lambda \geqslant 0$. Given some $\omega \in \mathbb{S}^2 \subset \mathbb{R}^3$, let us define

$$\psi_r(x_1, \dots, x_N) := \psi_1(x_1 - r\omega)\psi_{N-1}(x_2, \dots, x_N).$$

We have $\psi_r \in H^2(\mathbb{R}^{3N})$. Let us define

$$W_r(x_1, \dots, x_N) := \left(\sum_{j=1}^{M} Z_j |x_1 - R_j|^{-1} - \sum_{i=2}^{N} |x_1 - x_i|^{-1} \right) \psi_r(x_1, \dots, x_N).$$

Then $W_r \in L^2(\mathbb{R}^{3N})$, and we have

$$\begin{aligned} \|(H(N) - \lambda - E(N-1))\psi_r\| \leqslant{}& \|(H(N-1) - E(N-1))\psi_{N-1}\|\|\psi_1\| \\ &+ \|\psi_{N-1}\|\|(-\Delta - \lambda)\psi_1\| + \|W_r\|. \end{aligned}$$

From the fact that ψ_r converges pointwise to 0 as $r \to \infty$, we have that $\|W_r\| \to 0$ as $r \to \infty$, and therefore $\|(H(N) - \lambda - E(N-1))\psi_r\| \leqslant 3\varepsilon$ for r large enough. □

The elements of the spectrum $\sigma(H(N))$ lying strictly below the ionization threshold $\Sigma(N)$ are therefore isolated eigenvalues of finite multiplicity (that is, they belong to the discrete spectrum $\sigma_d(H(N)) := \sigma(H(N)) \setminus$

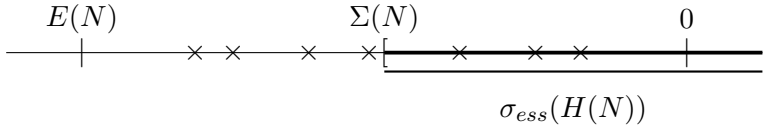

FIGURE 1. Possible picture for $\sigma(H(N))$.

$\sigma_{ess}(H(N))$). A stationary state associated with one of these eigenvalues is called a *bound state*. Note that, at this point, we cannot rule out the possibility of *embedded eigenvalues*, that is, eigenvalues lying within the essential spectrum. As we will see, it is nonetheless possible to prove that eigenvalues of $H(N)$ are non-positive, meaning that embedded eigenvalues, if any, are necessarily in the interval $[\Sigma(N), 0]$. From a mathematical perspective, we would think that such eigenvalues are physically as legitimate as the other ones. But the fact is they are highly artificial. Indeed, while $H(N)$ stands out as a perfect candidate within the boundaries of a mathematical laboratory, in the phenomenal world we truly are working with $\widetilde{H}(N) = H(N)+W$, where W is a morally small operator that accounts for all kinds of perturbations that are inherent to the scientific modelling and over which we have effectively no control. An elementary result from perturbation theory states that if W is small enough, the discrete spectrum of $\widetilde{H}(N)$ and $H(N)$ are essentially similar. But those eigenvalues that are embedded in the essential spectrum are very unstable with regard to W: they *generically* should not appear, *i.e.* only bound states are physically amenable quantum configurations. Embedded eigenvalues are linked to the phenomenon of quantum resonances [5, 13, 26, 32, 36].

Before we move on to the next section, let us quickly focus on the bound states of $H(N)$. Intuitively, the more electrons we add up in the vicinity of the nuclei (*i.e.* the bigger N), the less stable the system will tend to get, because electrons fiercely want to get far away from one another. Therefore, we expect that if N overshoots some threshold value N_c, bound states will simply cease to exist. On the other hand, if bound states do exist, we are in right to wonder how many are they. We summarize all the important results concerning bound states of $H(N)$ into one theorem:

Theorem 2. *Denote $Z_{tot} := \sum_{i=1}^{M} Z_i$ the total charge of the nuclei.*

- Rate of decay [29]. *Bound states of $H(N)$ have exponential decay.*
- Neutral and positively-charged molecules [43, 45]. *If $N \leqslant Z_{tot}$, there exists infinitely many bound states, meaning neutral and positively-charged molecules are always stable.*
- Negatively-charged molecules [35, 40, 42, 44]. *If $N > Z_{tot}$, then $H(N)$ has at most a finite number of bound states.*
- Very negatively-charged molecules [33, 34, 35] *There exists a critical N_c such that for all $N \geqslant N_c$, $H(N)$ has no bound states,* i.e. *$E(N-1) = E(N)$ and the molecule is instable.*

Idea of proof in the case $N \leqslant Z_{tot}$. We argue by induction on N. Using the *Courant-Fisher formula*, we want to prove that $\mu_k(H(N)) < \Sigma(N) = E(N-$

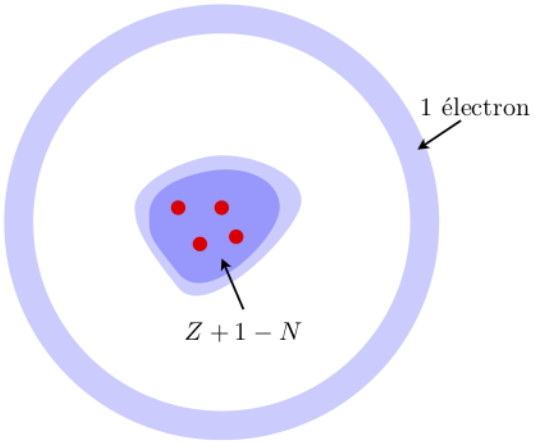

FIGURE 2. A heuristic picture of φ_n from [22]

1) for all k where we recall that

$$\mu_k(H(N)) := \sup_{\substack{W\subset H^2_a(\mathbb{R}^{3N})\\ \dim(W^\perp)=k}} \inf_{\substack{\psi\in W\\ \|\psi\|=1}} \langle \psi, H(N)\psi\rangle$$

is the k-th bound state of $H(N)$ counted with multiplicity. By introducing two cut-off functions, we build a sequence $(\varphi_n)_n$ such that φ_n represents a state of the system where $N-1$ electrons are kept in the vicinity of the nuclei and the remaining electron is sent at infinity (see figure Fig. 2). More precisely, we force the snatched electron e to remain localized in some ring $R(n) := B(0,Cn)\backslash B(0,cn)$ with $C, c > 0$ by imposing that the wave function of e belongs to some vector space $V \subset C_0^\infty(R(n))$ of dimension k, and that the other $N-1$ electrons are kept in $B(0,c'n)$ with $0 < c' < c$ in a state ψ_n with (we ignore the statistics)

$$\psi_n \propto \psi \prod_{i=1}^{N-1} \chi(x_i/n),$$

where $H(N-1)\psi = E(N-1)\psi$ and χ is a cut-off function such that $\mathrm{supp}(\chi) \subset B(0,c')$. Then, some simple but tedious calculations show that

$$\langle \varphi_n, H(N)\varphi_n\rangle = \langle \psi_n, H(N-1)\psi_n\rangle + \kappa\cdot\frac{N-(Z_{tot}+1)}{n} + O(n^{-2}),$$

for some positive constant $\kappa > 0$, and from the fact that ψ decay exponentially, one can prove that $\langle \psi_n, H(N-1)\psi_n\rangle = E(N-1) + o(n^{-2})$. □

1.3. **Bounds and asymptotics of N_c.** We are interested in the maximum number $N_c = N_c(Z)$ of electrons that can be bound to an atom (*i.e.* $M = 1$). It is a long standing open problem, sometimes referred to as the *ionization conjecture*, that $N_c \leqslant Z + C$, with C a constant, thought to be equal to 1 or 2. From Zhislin's result mentioned in the above theorem, we already now that $N_c \geqslant Z$, and we would like to find some upper bound on N_c. Let us recall briefly the present status of the conjecture.

It was first proved by Ruskai [33] and [34, 35] that N_c is not too large: in fact, Ruskai showed that $N_c = O(Z^{6/5})$ and Sigal showed that $N_c \leqslant 18Z$ and that $\overline{\lim}\, N_c(Z)/Z \leqslant 2$. A celebrated result of Lieb [24] proved that $N_c < 2Z+1$ for all $Z > 0$, which implies in particular that the ion H^{--} is not stable. The elegant and short proof is given below. It was recently given an improved bound when $Z \geqslant 6$ by Nam [28], namely $N_c < 1.22Z + 3Z^{1/3}$. Note that the ionization conjecture has already been proved in the context of Hartree-Fock [37] and Thomas-Fermi [6] models.

Theorem 3 (Lieb's bound)**.** *We have that* $N_c \leqslant 2Z+1$.

Proof. Here, statistics play no roles, *i.e.* the bound is still valid if we consider electrons to be bosons, so let us ignore it. Let $\psi \in H^2(\mathbb{R}^{3N})$ be a ground state of $H(N)$, i.e.

$$H(N)\psi = E(N)\psi. \tag{2}$$

Since ψ has exponential decay, $|x_N|\psi \in L^2(\mathbb{R}^{3N})$. Multiplying equation Eq. (2) by $|x_N|\overline{\psi}$, integrating over the entire space and taking the real part, we have $0 = \mathrm{Re}\langle |x_N|\psi, (H(N) - E(N))\psi\rangle$, which yields the estimate

$$\mathrm{Re}\langle |x_N|\psi, (-\Delta_{x_N})\psi\rangle - Z + \frac{1}{N}\underbrace{\sum_{1\leqslant i<j\leqslant N}\int_{\mathbb{R}^3\times\mathbb{R}^3}\frac{(|x_i|+|x_j|)|\psi(x)|^2|}{|x_i-x_j|}\mathrm{d}x}_{\geqslant N(N-1)/2} \leqslant 0,$$

where we used the symmetry of $(x_1,\dots,x_N) \mapsto |\psi(x_1,\dots,x_N)|^2$. Finally, as one can easily check,

$$\frac{|x_N|(-\Delta_{x_N}) + (-\Delta_{x_N})|x_N|}{2} = |x_N|^{1/2}\left(-\Delta_{x_N} - \frac{1}{4|x_N|^2}\right)|x|^{1/2} > 0,$$

where the last inequality is a direct consequence of Hardy's inequality, therefore we obtain the claimed estimate. □

Remark 4. This bound extends to the molecular setting (*i.e.* $M > 1$), with $N_c \leqslant 2Z_{tot} + M$ where $Z_{tot} = \sum_{i=1}^M Z_i$. See the original article of Lieb [24].

For large atoms, the asymptotic neutrality $\lim N_c(Z)/Z = 1$ was first proved by Lieb, Sigal, Simon and Thirring [**?**]. The proof relies on the construction of a well-chosen partition of unity. More precisely we divide the configuration space into $N+1$ pieces $A_0,\dots,A_N$, such that all the electrons in A_0 are close to the nucleus and A_i essentially consists of the region where the i-th particle has larger distance to the nucleus than any other electron, and we build an associated partition of unity $J_0,\dots,J_N$ such that $\mathrm{supp}(J_i) \subset A_i$. The localization error is proportional to $\sum_{i=0}^N \|\nabla J_i(x)\|^2$ and it is well controled in the regions. On A_0, the strong repulsion between electrons will dominate both the attraction by the nucleus and the localization error. On A_i, we split H_N into the $(N-1)$-body operator $H(N-1)$ corresponding to electrons $1,2,\dots,i-1,i+1,\dots,N$ and the additional terms due to the i-th electron. On A_i, the repulsion between the electron i and the other electrons dominates the attraction by the nucleus and the localization error if N is large enough. This asymptotic was latter improved to $N_c \leqslant Z + O(Z^{5/7})$ by Seco, Sigal and Solovej [**?**] and by Fefferman and Seco [**?**].

2. Singular spectrum & positive eigenvalues

In this section, we mention some important techniques to study the essential spectrum of a self-adjoint operator H. More precisely, those techniques will allow us to prove the absence of singular spectrum, and hence of embedded eigenvalues, on some portion of the essential spectrum of H. Applied to the electronic Hamiltonian $H(N)$, we are able to prove the absence of positive eigenvalues following the seminal article by Froese and Herbst [7]. We start by some physical consideration, heuristically explaining why one would strongly suspect that positive eigenvalues cannot exist.

2.1. **The virial theorem.**

Let us consider some general potential V vanishing at infinity (*i.e.* $V(x) \to 0$ as $|x| \to 0$). Classically, the only way to prevent a particle of positive energy from reaching infinity is to put up barriers. Therefore, from a classical perspective, we could expect bound states of positive energy to exist. But from the quantum perspective, because of *tunneling*, we would strongly suspect that such states simply cannot occur. As it turns out, this claim is actually wrong, and one can construct explicit potentials V such that $-\Delta + V$ has positive eigenvalues:

Example 4 (The Wigner-Von Neumann potential)**.** *Von Neumann and Wigner gave an example of a spherical and nonsingular potential V defined on the three-dimensional space $\mathbb{R}^3$ such that $\lambda = 1$ is an eigenvalue of $H = -\Delta + V$. By defining $g(r) = 2r - \sin 2r$, this potential is given by*

$$V(r) = \frac{-32 \sin r \left[g(r)^3 \cos r - 3g(r)^2 \sin^3 r + g(r) \cos r + \sin^3 r \right]}{\left[1 + g(r)^2\right]^2},$$

where $r = |x|$. This complicated V is seen to be bounded and to vanish at infinity (with asymptotics $V(r) = -8 \sin r / r + O(r^{-2})$), so that the Schrödinger operator H is self-adjoint on $H^2(\mathbb{R}^3)$ with $C_0^\infty(\mathbb{R}^3)$ as a core, and $\sigma_{ess}(H) = [0, \infty)$. Tedious computations show that H has an eigenvalue at $\lambda = 1$ with eigenvector

$$\psi(r) = \frac{\sin r}{r \left[1 + g(r)\right]} \in H^2(\mathbb{R}^3).$$

While this example seems rather pathological, it does pertain to physics. Indeed, the critical aspect of V is its oscillations, *i.e.* it was fashioned so that reflections across bumps adds up in a coherent manner. But in the case of the Coulomb potential, as there are no oscillations whatsoever, we shall remain strongly convinced that $H(N)$ has no positive eigenvalues.

An important tool to control positive eigenvalues in the *virial theorem*, that relates kinetic energy to potential energy. Defining $A = \frac{i}{2}(x \cdot \nabla + \nabla \cdot x)$ the infinitesimal generator of dilation, that we recall to be self-adjoint on $D(A) = \{u \in L^2(\mathbb{R}^3) : x \cdot \nabla u \in L^2(\mathbb{R}^3)\}$ with $C_0^\infty(\mathbb{R}^3)$ as a core, we formally have that $i[H, A] = 2H - (x \cdot \nabla V + 2V)$. Let λ be an eigenvalue of H and ψ a corresponding eigenvector. The fact that H is a symmetric operator implies $\langle \psi, i[H, A]\psi \rangle = 0$. Therefore, one has

$$2\lambda \|\psi\|^2 = \langle \psi, (x \cdot \nabla V + 2V)\psi \rangle.$$

Suppose there exist $\gamma \in (0,2)$ and $\lambda_0 \in \mathbb{R}$ such that $x\cdot\nabla V+\gamma V \leqslant \gamma\lambda_0$, which ought to be understood as some sort of upper bound on the oscillations of V. Then one has

$$\begin{aligned}\gamma\lambda_0\|\psi\|^2 &\geqslant \langle\psi,(x\cdot\nabla V+\gamma V)\psi\rangle\\ &= \underbrace{(2-\gamma)\|\nabla\psi\|^2}_{>0}+\gamma\lambda\|\psi\|^2,\end{aligned}$$

yielding that H has no eigenvalues in $[\lambda_0,\infty)$. The problem with this attractive argument is that an eigenvector ψ of H will not necessarily have the property that $A\psi$ lies in the domain of H or that ψ belongs to the domain of A. Although one envisages eigenvectors as decaying exponentially, those eigenvalues embedded in the essential spectrum may fall off so poorly that $x\cdot\nabla\psi$ could fail to be in $L^2(\mathbb{R}^3)$. Let us state and prove a first rigorous version of the virial theorem:

Theorem 5 (Virial theorem I)**.** *Let V be a real multiplication operator on $L^2(\mathbb{R}^n)$ that is $-\Delta$-bounded with bound less than one (*i.e. *so that $H=-\Delta+V$ is self-adjoint on $D(-\Delta)$). Suppose there exists a multiplication operator W on $L^2(\mathbb{R}^n)$ with $D(W)\supset D(-\Delta)$ so that for every $\psi\in D(-\Delta)$,*

$$(a-1)^{-1}\left[V(ax)-V(x)\right]\psi \xrightarrow[a\to 1]{} W\psi. \tag{3}$$

Then if λ is a real eigenvalue of $-\Delta+V$ with $\psi\in D(-\Delta)$ a corresponding eigenvector, we have the equality $\langle\psi,-\Delta\psi\rangle=\frac{1}{2}\langle\psi,W\psi\rangle$.

Proof. We write $V_a(x)=V(ax)$. If $\psi\in D(-\Delta)$ is an eigenvector of $-\Delta+V$ with eigenvalue $\lambda\in\mathbb{R}$, then ψ_a is an eigenvector for the scaled Schrödinger operator $-\Delta+a^2V_a$ with eigenvalue $a^2\lambda$. It easily follows from the symmetry of $-\Delta$ and self-adjointness of $-\Delta+V$ that for all a,

$$(a+1)\langle\psi_a,V_a\psi\rangle+(a-1)^{-1}\langle\psi_a,(V_a-V)\psi\rangle=\lambda(a+1)\langle\psi_a,\psi\rangle.$$

By taking the limit as $a\to 1$, the theorem follows. □

Remark 5. The operator W is nothing but $x\cdot\nabla V$ is the distributional sense. Moreover, the strong limit Eq. (3) is usually proven in the following way: if there exists a couple of functions W and $\widetilde{W}$ such that $(a-1)^{-1}[V(ax)-V(x)]$ converges pointwise to W as $a\to 1$ and $\left|(a-1)^{-1}[V(ax)-V(x)]\right|\leqslant\widetilde{W}$ with $D(\widetilde{W})\supset D(-\Delta)$, then Eq. (3) follows from the dominated convergence theorem.

Corollary 6 (Virial theorem for homogeneous potentials)**.** *Let V be a real multiplication operator on $L^2(\mathbb{R}^n)$ that is $-\Delta$-bounded with bound less than one. Suppose that V is homogeneous of degree $-\alpha$ with $0<\alpha<2$ (*i.e. *$V(ax)=a^{-\alpha}V(x)$). Then $-\Delta+V$ has no positive eigenvalues. In particular, the Hamiltonian of the hydrogen atom (*i.e. *$H=-\Delta-\frac{1}{|x|}$) has no positive eigenvalues.*

Remark 6. Another way to think about the virial theorem is from a dynamical perspective. Indeed, given some operator A and $\psi=\psi(t,x)$ a solution to the Schrödinger equation $i\hbar\partial_t\psi=H\psi$, we (formally) have that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t),A\psi(t)\rangle=\langle\psi(t),[H,iA]\psi(t)\rangle.$$

Thus, if $\psi(t) = e^{-itH}\psi$ with ψ an eigenvector of H, we have $\langle \psi, [H, iA]\psi\rangle = 0$. In other words, one might think of the virial theorem as a special case of the so-called quantum mechanics *Ehrenfest theorem*.

2.2. **Some techniques to study the continuous spectrum.**

2.2.1. *LAP & positive commutators techniques (1).* Let H be a self-adjoint operator in a Hilbert space $\mathcal{H}$, and $R(z) = (H - z)^{-1}$ its resolvent defined for every $z \in \mathbb{C} \setminus \sigma(H)$. For $\lambda \in \sigma(H)$, we have that $\|R(\lambda + i\mu)\| = |\mu|^{-1}$, which implies that $R(\lambda + i\mu)$ cannot have limits in $B(\mathcal{H})$ the $C^\star$-algebra of bounded operators over $\mathcal{H}$ as $|\mu| \to 0$. However, for certain vectors $\varphi \in \mathcal{H}$, the function $F(z) = \langle \varphi, R(z)\varphi\rangle$, which is analytic over $\mathbb{C} \setminus \sigma(H)$, could have a limit as $z \to \lambda$ from the upper or lower half-plane. If this happens for sufficiently many φ one can infer results on the spectral properties of H. This fondamental idea stems from the *limiting absorption principle*, which is the object of the following proposition :

Proposition 7 (Limiting absorption principle (LAP))**.** *Let H be a self-adjoint operator over $\mathcal{H}$, and $R(z) = (H - z)^{-1}$ its resolvent defined for every $z \in \mathbb{C} \setminus \sigma(H)$. Suppose there exists some dense set $D \subset \mathcal{H}$ such that for every $\varphi \in D$, there is a constant $C(\varphi) < \infty$ so that*

$$\overline{\lim_{\mu \to 0}} \sup_{\lambda \in (a,b)} \langle \varphi, \operatorname{Im} R(\lambda + i\mu)\varphi\rangle < C(\varphi).$$

Then H has purely absolutely continuous spectrum in (a, b).

Proof. By *Stone's formula* (see [22] for instance), one has

$$\frac{1}{2}\langle \varphi, (\mathbb{1}_{[a',b']}(H) + \mathbb{1}_{(a',b')}(H))\varphi\rangle = \lim_{\mu \to 0} \frac{1}{\pi} \int_{a'}^{b'} \langle \varphi, \operatorname{Im} R(\lambda + i\mu)\varphi\rangle d\lambda.$$

This implies immediately that for all $(a', b') \subset (a, b)$, one has

$$\langle \varphi, \mathbb{1}_{(a',b')}(H)\varphi\rangle \leqslant \frac{1}{\pi} C(\varphi)|b' - a'|.$$

This, in turn, implies that for every Borel set $\Omega \subset (a, b)$, one has $\langle \varphi, \mathbb{1}_\Omega(H)\varphi\rangle \leqslant \frac{1}{\pi} C(\varphi)|\Omega|$, where $|\cdot|$ denotes the Lebesgue measure on the real line. □

Let us present a first result that will allow us to prove that the spectrum of a general self-adjoint operator H is absolutely continuous on some open interval $\mathcal{I} \subset \mathbb{R}$, and therefore has no eigenvalues in $\mathcal{I}$:

Theorem 8 (Putnam)**.** *Let H and A be bounded and self-adjoint operators, such that $i[H, A] = C^\star C$, where $Ker(C) = \{0\}$. Then H has a purely absolutely continuous spectrum.*

Proof. For every $O \in B(\mathcal{H})$, recall that $\|O^\star O\| = \|O\|^2$. Thus,

$$\begin{aligned}\|CR(\lambda \pm i\mu)\|^2 &= \|R(\lambda \mp i\mu)i[H - \lambda \mp i\mu, A]R(\lambda \pm i\mu)\| \\ &\leqslant \|AR(\lambda \pm i\mu)\| + \|R(\lambda \mp i\mu)A\| + 2\mu\|R(\lambda \mp i\mu)AR(\lambda \pm i\mu)\| \\ &\leqslant 4\mu^{-1}\|A\|\end{aligned}$$

Then

$$\|C \operatorname{Im} R(\lambda + i\mu) C^\star\| = \|C \underbrace{\frac{R(\lambda + i\mu) - R(\lambda - i\mu)}{2i}}_{i\mu R(\lambda+i\mu)R(\lambda-i\mu)} C^\star\| \leqslant 4\|A\|$$

Since $ran(C^\star)$ is dense, we conclude using the limiting absorption principle. □

This result, while very nice, has a major flaw. Indeed, the hypotheses of Putnam's theorem are too artificial to be of any use in studying the essential spectrum of $H(N)$, starting from the very fact that $H(N)$ is not even a bounded operator. In what follows, we shall try to investigate some techniques to overcome this issue and to drastically weaken the hypotheses required on H and A.

Remark 7. Putnam's theorem gives us a peak at *positive commutators techniques*. Let us give a heuristic explanation of why these techniques are powerful to study the singular continuous spectrum of an operator. We use the famous *Heisenberg picture*: given a state ψ and $\psi(t) := e^{-itH/\hbar}\psi$ its evolution at time t under the dynamic generated by the Hamiltonian H, one can take a look at the Heisenberg picture

$$\mathcal{H}_\psi(t) := \langle \psi(t), A\psi(t) \rangle,$$

for some observable A. Formally, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{H}_\psi(t) = \langle \psi(t), [H, iA]\psi(t) \rangle. \tag{4}$$

Therefore, if $[H, iA] \geqslant \alpha > 0$, we have that $\mathcal{H}_\psi(t) \geqslant \mathcal{H}_\psi(0) + \alpha t\|\psi\|^2$, which may be a strong indicator that dispersion is taking place with respect to A. Hence, purely absolutely continuous spectrum is expected. If H and A verify the hypotheses of Theorem 8, then we have

$$\mathcal{H}_\psi(t) \geqslant \mathcal{H}_\psi(0) + \int_0^t \|Ce^{-itH/\hbar}\psi\|^2 \mathrm{d}t.$$

2.2.2. *Posivitive commutator techniques & Mourre's theory (2).* In the beginning of the 80's, Eric Mourre from the Centre de Physique Théorique de Marseille Luminy had the brilliant insight [27] that the rather demanding hypotheses on H and the commutator $[H, iA]$ required in Putnam's theory and more generally in the conjugate operator method (see below) could be drastically weaken, provided that $[H, iA]$ had a definite sign when localized in energy. In more precise terms, his condition was as follows: given some $\lambda \in \sigma(H)$, there are real numbers $c > 0$, $\delta > 0$ and some compact operator K such that

$$\mathbb{1}_{\mathcal{I}}(H)[H, A]\mathbb{1}_{\mathcal{I}}(H) \geqslant c\mathbb{1}_{\mathcal{I}}(H) + K, \tag{5}$$

with $\mathcal{I} := (\lambda - \delta, \lambda + \delta)$. This inequality is called a *Mourre estimate for H at λ*. If $K = 0$, we call it a *strict* Mourre estimate. Note that, if H and A are bounded operator, the commutator on the l.h.s of Eq. (5) is easily understood in the canonical way as $[H, A] := HA - AH$. But in the more general setting where H and A are not bounded (as they will be in practice),

the estimate Eq. (5) should be understood in the sense of sesquilinear form on $D(A) \cap D(H)$. We slightly get into these technicalities in what follows. Readers interested in a more complete approach might find their happiness in [1, 10, 12, 15, Golénia].

Given H and A two self-adjoint operators, we say that A *is conjugated to* H if the following are verified:

(i) $D(A) \cap D(H)$ is a core for H
(ii) For every $\varphi \in D(H)$, we have $\sup_{|t|\leqslant 1} \|H \exp(itA)\varphi\| < \infty$
(iii) $[H, A]$ extends to a bounded operator $D(H) \to D(H)'$, written $[H, A]^0$
(iv) $e^{itA} D(H) \subset D(H)$ for all $t \in \mathbb{R}$.

Remark 8. We recall that $[H, A]$ is defined as a sesquilinear form on $D(A) \cap D(H)$ by

$$\langle \psi, [H, A]\varphi \rangle := \langle H\psi, A\varphi \rangle - \langle A\psi, H\varphi \rangle$$

for all $\psi, \varphi \in D(A) \cap D(H)$. Therefore, the operator $[H, A]^0 : D(H) \to D(H)'$ is defined using *Riesz lemma*, and one easily checks that

$$[H, A]^0 \psi = \lim_{\tau \to 0} [H, A_\tau]\psi, \tag{6}$$

for all $\psi \in D(H)$, where $A_\tau := (i\tau)^{-1}(e^{i\tau H} - 1)$. From hypothesis *(iv)*, we are allowed to define the commutator $[H, A_\tau]$ is the canonical way. Hypotheses *(i)* and *(iii)* naturally appear in the proof of Eq. (6) as one must use density arguments to cope with the non-explicit extension $[H, A]^0$. Hypothesis *(ii)*, less obvious, allows us to commute limits.

Under these hypotheses, the l.h.s of the estimate Eq. (5) is a well-defined operator $D(H) \to D(H)$. Note that there is a more elegant and less verbose way to sum up those hypotheses, which is that H belongs to $C^1(A)$, that is to say that for any $z \in \mathbb{C} \setminus \sigma(H)$ (and therefore for all), the function $\mathbb{R} \ni t \mapsto e^{itA}(H - z)^{-1} e^{-itA}\psi$ is C^1 in the classical sense for all $\psi \in \mathfrak{h}$.

If A is conjugated to H, we can state a more abstract version of the virial theorem:

Theorem 9 (Virial theorem II)**.** *Let H and A be a self-adjoint operators such that A is conjugated to H. If ψ is an eigenvector of H, then $\langle \psi, [H, A]^0 \psi \rangle = 0$.*

Proof. If $H\psi = E\psi$, then

$$\begin{aligned} \langle \psi, [H, A]^0 \psi \rangle &= \lim_{\tau \to 0} \langle \psi, [H, A_\tau]\psi \rangle \\ &= E \lim_{\tau \to 0} (\langle \psi, A_\tau \psi \rangle - \langle A_{-\tau}\psi, \psi \rangle) \\ &= 0. \end{aligned}$$

□

Proposition 10. *Let H and A be self-adjoint operators such that A is conjugated to H. Suppose the strict Mourre's estimate Eq. (5) (*i.e. *$K = 0$) holds on $\mathcal{I}$. Then H has no eigenvalues in $\mathcal{I}$.*

Proof. Suppose that H has an eigenvalue $\gamma \in \mathcal{I}$. Then, there exists $\psi \in D(H) \setminus \{0\}$ such that $H\psi = \gamma\psi$. From the virial theorem and the fact that $\mathbb{1}_{\mathcal{I}}(H)\psi = \psi$, one has $\langle \psi, [H, A]^0\psi \rangle = 0 \geqslant c\|\psi\|^2$. Since $c > 0$, we must have $\|\psi\|^2 = 0$, which is a contradiction. □

Proposition 11. *Let H and A be self-adjoint operators such that A is conjugated to H. Suppose the Mourre's estimate Eq. (5) holds on $\mathcal{I}$. Then H has a finite number of eigenvalues in $\mathcal{I}$, and they are all of finite multiplicity.*

Proof. Suppose that $(\psi_n)_n$ is a sequence of orthonormal eigenvectors for H with energies in $\mathcal{I}$. From the virial theorem, we have $0 \geqslant c + \langle \psi_n, K\psi_n \rangle$. Since $\psi_n \rightharpoonup 0$, we have that $(Kf_n)_n$ converges to 0, which yields a contradiction since $c > 0$. □

2.2.3. *The conjugate operator method.* Coming back to the LAP, one way of checking that the limit of $F(\lambda + i\mu)$ exists as $\mu \to 0$ is to prove that $\int_0^1 |\partial_\mu F(\lambda + i\mu)| \, \mathrm{d}\mu < \infty$. A standard technique for obtaining the finiteness of such integrals is to establish an estimate for $\partial_\mu F(\lambda + i\mu)$ in terms of $F(\lambda + i\mu)$, and then to use some version of the *Gronwall lemma*. As a first example, let us consider some arbitrary (unbounded) operator A. Since $R'(z) = R(z)^2$, we formally have that $[A, R(z)] = R(z)[A, H]R(z)$. Suppose that $\boxed{i[H, A] = H}$, hence we have $zR'(z) = i[A, R(z)] - R(z)$, so that if we assume $\varphi \in D(A)$, we obtain $zF'(z) = -F(z) - \langle iA\varphi, R(z)\varphi \rangle - \langle R(z)\varphi, iA\varphi \rangle$. If $z = \lambda + i\mu$ with $\mu > 0$, then $\|R(z)\varphi\| = \|R(\overline{z})\varphi\| = \mu^{-\frac{1}{2}} |\operatorname{Im} F(z)|^{\frac{1}{2}}$. Hence, if $\lambda \neq 0$, we get that

$$|\partial_\mu F(\lambda + i\mu)| \leqslant |\lambda|^{-1}(\|\varphi\| + 2\|A\varphi\|)\mu^{-\frac{1}{2}} \, |F(\lambda + i\mu)|^{\frac{1}{2}} \, .$$

Since $F(z) \neq 0$ if $\operatorname{Im} z \neq 0$, by dividing both sides by $|F(\lambda + i\mu)|^{\frac{1}{2}}$ and integrating the resulting inequality, we have that for every $0 < \mu < 1$,

$$|F(\lambda + i\mu)|^{\frac{1}{2}} \leqslant |F(\lambda + i)|^{\frac{1}{2}} + |\lambda|^{-1} \left(\|\varphi\| + 2\|A\varphi\|\right).$$

Thus, for each $\eta > 0$, there exists a constant K_η such that for every $|\lambda| \geqslant \eta$, we have

$$|\partial_\mu F(\lambda + i\mu)| \leqslant \frac{K_\eta}{\sqrt{\mu}} \left(\|\varphi\|^2 + \|A\varphi\|^2\right),$$

which implies the existence of $\lim_{\mu \to 0^+} F(\lambda + i\mu)$ uniformly in $|\lambda| \geqslant \eta$.

This powerful technique (*i.e.* so called *conjugate operator method*) requires to find a well-chosen operator A such that $i[H, A] = H$. Suppose we rather have that H and A are bounded operators such that there exists $\alpha > 0$ with $i[H, A] \geqslant \alpha$. This implies $R'(z) \leqslant \alpha^{-1}[A, R(z)]$. Thus $F'(z) \leqslant \alpha^{-1}(\langle iA\varphi, R(z)\varphi \rangle - \langle R(z)\varphi, iA\varphi \rangle)$. Therefore

$$|\partial_\mu F(\lambda + i\mu)| \leqslant \alpha^{-1}\|A\varphi\|\mu^{-\frac{1}{2}}|F(\lambda + i\mu)|^{\frac{1}{2}},$$

which leads to the same conclusion as previously, once again advocating for the use of positive commutators techniques.

Before moving on to the next section, let us just notice that the terminology here is not innocuous. If A is a conjugate operator for H, the formal manipulation that were done above are justified, for we have:

Lemma 12. *If A is conjugated to H, then*

$$[A, R(z)] = R(z)[A, H]R(z)$$

in the sense of form on $\mathfrak{h} \times \mathfrak{h}$.

2.3. **Application : absence of positive eigenvalues for $H(N)$.** Let us come back to our initial question of whether or not $H(N)$ has positive eigenvalues. We have indicated in the very beginning of this note that in fact it does not, and we shall now proceed to give an informal proof of this statement. It was the seminal works of Froese and Herbst [7, 8, 9] as well as Perry, Sigal and Simon [30] that had answered this longed-for problem.

We consider a class of Schrödinger operators actually somewhat larger than the class of N-body Hamiltonians arising in physics. Let $\{\pi_i\}_{i\in I}$ be a set of (orthogonal) projections onto the subspaces $\{X_i\}_{i\in I}$ of $\mathbb{R}^n$. Suppose V_i is a real-valued function of $x_i \in X_i$ which satisfies some conditions to be mentioned after, and consider the self-adjoint operator H densily-defined over $L^2(\mathbb{R}^2)$ with $D(H) = D(-\Delta)$ as

$$H = -\Delta + \underbrace{\sum_{i\in I} V_i(\pi_i(x))}_{:=V}.$$

The two sets of conditions on V_i in what follows are:

(i) For every $i \in I$, $V_i(\Delta_{x_i} + 1)^{-1}$ and $(\Delta_{x_i} + 1)^{-1} x_i \cdot \nabla V_i (\Delta_{x_i} + 1)^{-1}$ are compact operators over $L^2(X_i)$.

(ii) Let $\nu_i = \dim(X_i)$ and $p_i = \max(2, \nu_i - 1)$. Then, $V_i \in L^{p_i}(X_i) + L^\infty(X_i)$ and $V_i = V_i^{(1)} + V_i^{(2)}$ such that $(1 + |x_i|)V_i^{(1)} \in L^{p_i}(X_i) + L^\infty(X_i)$ and $x_i \cdot \nabla V_i$ is infinitesimally $(-\Delta_{x_i})$-bounded.

We defined as *threshold* any eigenvalue of $H_J = -\sum_{j\in J} \Delta_{x_j} + \sum_{j\in J} V_j(\pi_j(x))$ where J is a proper subspace of I and denote $\mathcal{T}(H)$ the set of thresholds of H. Suppose ψ is an eigenvector of H for the energy E, *i.e.* $\psi \in D(H)$ and $H\psi = E\psi$. We ask the question: when is $\exp(\alpha|x|)\psi \in L^2(\mathbb{R}^n)$? Reminiscent of this question, we define $\tau(\psi)$ to be

$$\tau(\psi) = \sup\{\alpha^2 + E : \alpha \geqslant 0,\ \exp(\alpha|x|)\psi \in L^2(\mathbb{R}^n)\}.$$

We have the following two theorems:

Theorem 13. *If V_i satisfies condition* (i) *for all $i \in I$, then $\tau(\psi) \in \mathcal{T}(H) \cup \{\infty\}$.*

Theorem 14. *If V_i satisfies condition* (ii) *for all $i \in I$, then $\tau(\psi) \neq \infty$.*

Theorem 13 gives an L^2 upper bound to ψ, namely if τ_0 is the first threshold at or above E, then $\exp(\alpha|x|)\psi \in L^2(\mathbb{R}^n)$ for all $\alpha < \sqrt{\tau_0 - E}$. Theorem 14 eliminates the possibility that $\tau(\psi) = \infty$, meaning there must exist a threshold above E. By induction, it then follows easily that:

Corollary 15. *If V_i satisfies condition* (i) *and* (ii) *for all $i \in I$, then H has no positive thresholds or eigenvalues.*

Corollary 16. *If V_i satisfies condition* (i) *and* (ii) *for all $i \in I$, then $\exp(\alpha|x|)\psi \notin L^2(\mathbb{R}^n)$ for all $\alpha > \sqrt{-E}$.*

Let us roughly sketch the proof of Theorem 13. If $A = \frac{1}{2}(x\cdot\nabla+\nabla\cdot x)$ is the infinitesimal generator of dilation, condition (i) implies that the commutator $[H, A]$ is well-defined and that $[H, A] = 2(-\Delta) + x \cdot \nabla V$ as in the virial theorem. The first ingredient in the proof is the Mourre estimate first proved for N-body by Perry, Sigal, and Simon [**?**]. It says that if τ is a non-threshold point then there exists an open interval $\mathcal{I}$ containing τ such that Eq. (5) is verified. The second ingredient is some equations satisfied by $\psi_F := exp(F)\psi$ where F is an increasing function of $|x|$. A computation shows that

$$H\psi_F = (E + (\nabla F)^2)\psi_F - B\psi_F,$$

with $B = \nabla F \cdot \nabla + \nabla \cdot \nabla F$. By denoting $\widetilde{A} = \exp(F)A\exp(F)$, a formal computation shows that $\langle\psi, [H, \widetilde{A}]\psi\rangle = 0$, so that

$$\langle\psi_F, [H, A]\psi_F\rangle = -4\|g^{1/2}A\psi_F\|^2 + \langle\psi_F, G\psi_F\rangle,$$

where G is a function that is small for large $|x|$ and g is defined such that $\nabla F = xg$. We now can already prove that $\tau(\psi)$ cannot be a non-thresold point above E. Indeed, assumer the contrary, so that one can find $\alpha > 0$ with $\alpha^2 + E < \tau(\psi) < (\alpha+\gamma)^2 + E$ where α and γ are such that the Mourre estimate holds for some open interval $\mathcal{I} \subset [\alpha^2+E, (\alpha+\gamma)^2+E]$. By definition, we know that $\exp(\alpha|x|)\psi \in L^2(\mathbb{R}^n)$ and $\exp((\alpha+\gamma)|x|)\psi \notin L^2(\mathbb{R}^n)$. We interpolate between those two situations by defining F_λ as

$$\exp(F_\lambda) = \exp(\alpha|x|)(1 + \gamma|x|/\lambda)^\lambda.$$

Then, $\exp(F_\lambda)\psi \in L^2(\mathbb{R}^n)$ for all λ but we have that $\lim_{\lambda\to\infty} \|\exp(F_\lambda)\psi\| = \infty$. Therefore, defining $\Psi_\lambda = \exp(F_\lambda)\psi/\|\exp(F_\lambda)\psi\|$, we have that $\Psi_\lambda \rightharpoonup 0$ as $\lambda \to \infty$ as one easily checks that $\int_B |\Psi_\lambda|^2 \to 0$ as $\lambda \to \infty$ for every bounded Borel-set $B \subset \mathbb{R}^n$. The next step is then to prove that $B\Psi_\lambda \rightharpoonup 0$ as $\lambda \to \infty$, which, from the fact that $(\nabla F)^2$ is approximately α^2, gives us for large λ

$$H\Psi_\lambda \approx (E + \alpha^2)\Psi_\lambda,$$

which, roughly speaking, means that Ψ_λ is within the range of $\mathbb{1}_\mathcal{I}$. From the Mourre estimate, we have

$$\langle\Psi_\lambda, \mathbb{1}_\mathcal{I}[H, A]\mathbb{1}_\mathcal{I}\Psi_\lambda\rangle \geqslant c\|\mathbb{1}_\mathcal{I}\Psi_\lambda\|^2 + \langle\Psi_\lambda, K\Psi_\lambda\rangle.$$

At the limit, we can ignore $\mathbb{1}_\mathcal{I}$, and by compactness of K, we have

$$\varliminf_{\lambda\to\infty} \langle\Psi_\lambda, \mathbb{1}_\mathcal{I}[H, A]\mathbb{1}_\mathcal{I}\Psi_\lambda\rangle \geqslant c > 0.$$

But on the other hand, we know that $\langle\Psi_\lambda, [H, A]\Psi_\lambda\rangle \leqslant \langle\Psi_\lambda, G\Psi_\lambda\rangle$. For large λ, Ψ_λ moves to regions where $|x|$ is large, and therefore regions where G is small (say of order γ), we have

$$\varlimsup_{\lambda\to\infty} \langle\Psi_\lambda, \mathbb{1}_\mathcal{I}[H, A]\mathbb{1}_\mathcal{I}\Psi_\lambda\rangle \leqslant 0,$$

which yields the final contradiction for small enough γ.

Remark 9. From that we conclude that $H(N)$ has no positive eigenvalues. Indeed, here $V_i(x) = V = |x|^{-1}$ essentially. Condition (ii) is trivially satisfied. Condition (i) follows from the fact that

$$V(-\Delta+1)^{-1} = \underbrace{|x|^{-1}\mathbb{1}_{B(0,R)}(-\Delta+1)^{-1}}_{\text{compact}} + \underbrace{|x|^{-1}\mathbb{1}_{B^c(0,R)}(-\Delta+1)^{-1}}_{\text{bounded of norm } \leqslant 1/R},$$

meaning that $V(-\Delta+1)^{-1}$ is compact as limit of compact operators.

3. What about eigenvalues in $[\Sigma(N), 0]$?

From the previous section, we know that embedded eigenvalues, if any, are located in the interval $[\Sigma(N), 0]$. We mentioned earlier that those eigenvalues were highly non-generic:

Example 17. *Consider the Hamiltonian of the Helium atom $H = H_0 + |x_1 - x_2|^{-1}$, with*

$$H_0 = -\Delta_{x_1} - \frac{2}{|x_1|} - \Delta_{x_2} - \frac{2}{|x_2|}.$$

We can rewrite $H_0 = 1 \otimes h + h \otimes 1$ with $h = -\Delta - 2|x|^{-1}$ densely-defined over $L^2(\mathbb{R}^3)$. The eigenvalues of h are explicitly known to be $\{-1/n^2\}_{n\in\mathbb{N}}$, are therefore the eigenvalues of H_0 are given by $\{-(1/n^2 + 1/m^2)\}_{n,m\in\mathbb{N}}$ [31]. Moreover, we know that $\sigma_{ess}(h) = [0,\infty)$, so that $\sigma_{ess}(H_0) = [-1,\infty)$. Hence, embedded eigenvalues do exist for the reduced Hamiltonian H_0. When the internal potential V, seen a perturbation term, is turned on, those eigenvalues will dissolve [32].

Embedded eigenvalues are touchy business. For a primer, contrary to the eigenvalues lying below the essential spectrum, we cannot access them easily (*i.e.* there is no such thing as a Courant-Fischer formula for them). While the critical N_c we talked about in the first section dealt with the absence of bound states, we now wonder about the existence of a critical value $\widetilde{N}_c$ such that, for all $N \geqslant \widetilde{N}_c$, $H(N)$ has no eigenvalues at all. In their paper [23], Lewin and Lenzmann proved that $\widetilde{N}_c$ not only exists, but that it is bounded above by $4Z+1$ in the atomic case (*i.e.* $M = 1$). We first present the proof of the authors before extending the bound to the molecular setting.

3.1. Upper bound for $\widetilde{N}_c$ in the atomic setting.

3.1.1. *Heuristic.* The proof is based on a novel positive commutator argument. In their paper, the authors were mainly interested in the long-time behavior of atoms in the Hartree model, as they showed that after a long period of time, the average number of electrons in any finite ball around the nucleus is always smaller that $4Z$. The following bound on $\widetilde{N}_c$ came in as a happy byproduct:

Theorem 18. *The atomic Hamiltonian $H(N)$ (*i.e. *with $M = 1$) has no eigenvalues when $N \geqslant 4Z+1$.*

Let us first explain the general strategy of the proof. We write for simplicity $p := -i\nabla$ the impulsion operator, so that we abuse the notation $p^2 = -\Delta$.

For a (smooth, compactly supported) function f defined over $\mathbb{R}^3$, we denote A_f its corresponding *virial operator*, *i.e.*

$$A_f := p \cdot \nabla f + \nabla f \cdot p.$$

For a generic operator N-body Schrödinger operator

$$H = -\Delta + \sum_i V(x_i) + \frac{1}{2}\sum_{i \neq j} w(x_i - x_j),$$

and $\psi(t) = \psi(x,t)$ a solution to the Schrödinger equation $i\hbar\partial_t\psi = H\psi$, one (formally) has

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle\psi(t), f\psi(t)\rangle = \overbrace{\left\langle\psi(t), i[p^2, A_f]\psi(t)\right\rangle}^{\gamma_k} - 2\overbrace{\left\langle \psi(t), \nabla f \cdot \nabla\left(\sum_i V(x_i)\right)\psi(t)\right\rangle}^{\gamma_p} - \underbrace{\left\langle \psi(t), \nabla f \cdot \nabla\left(\sum_{i\neq j} w(x_i - x_j)\right)\psi(t)\right\rangle}_{\gamma_w} \tag{7}$$

If ψ is a stationary state, the l.h.s of Eq. (7) is conveniently zero, leading to the equation $\gamma_k - 2\gamma_p - \gamma_w = 0$. If the virial function f is carefully chosen so that $\nabla f \cdot \nabla V = 1$, rearranging Eq. (7) yields $N = \frac{1}{2}(\gamma_k - \gamma_w)$. This last equation is of interest for us because it relates N to quantities that emanates from the very wave function ψ. In the atomic case, by letting $f(x) = \sum_{i=1}^N |x_i|^3/3$, we are (formally) lead to

$$2ZN = \langle\psi(t), i[-\Delta, A_{|x|^3}]\psi(t)\rangle + \sum_{i\neq j}\int_{\mathbb{R}^3\times\mathbb{R}^3}(|x_i|x_i - |x_j|x_j)\cdot\frac{x_i - x_j}{|x_i - x_j|^3}|\psi(t,x)|^2\mathrm{d}x.$$

The first key observation then made by the authors is the positivity of the commutator

$$\gamma_k = [-\Delta, A_{|x|^3}] = [-\Delta, [-\Delta, |x|^3] \geqslant 0, \tag{8}$$

and secondly that $(|x|x - |y|y)\cdot\frac{x-y}{|x-y|^3} \geqslant \frac{1}{2}$ for all $x \neq y \in \mathbb{R}^3$, so that $-\gamma_w \geqslant \frac{1}{2}N(N-1)$, hence yielding the announced bound $\widetilde{N_c} \leqslant 4Z + 1$.

Remark 10. In other words, given $\psi = \psi(x,t)$ a solution to the Schrödinger equation Eq. (1), we have that

$$\frac{1}{3}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\int_{\mathbb{R}^3}|x|^3|\psi(x,t)|^2\mathrm{d}x \geqslant \frac{1}{2}N(N - 4Z - 1) > 0 \tag{9}$$

if $N > 4Z + 1$, meaning that the quantity $\frac{1}{3}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathbb{R}^3}|x|^3|\psi(x,t)|^2\mathrm{d}x$ grows at least like t^2 as $t \to \infty$. This growth is a strong indication that not all the electrons can bind to the nuclei and that some of them have to escape to infinity.

Remark 11. This method extends to the time-dependant nonlinear Hartree equation

$$i\hbar\frac{\partial}{\partial t}u(x,t) = \left(-\Delta - \frac{Z}{|x|} + |u|^2 \star \frac{1}{|x|}\right)u(x,t), \tag{10}$$

where it shows that $\widetilde{N_c} \leqslant 4Z$. Note that virial or positive commutator arguments are very common in the literature. When $|x|^3$ is replaced by $|x|$, we are lead to the famous *Morawetz-Lin-Strauss estimate* for nonlinear Schrödinger equations. Unfortunately, due to purely attractive term $-Z/|x|$ in Hartree equation Eq. (10), *a priori* this estimate does not yield any dispersive information about $u(x,t)$.

3.1.2. *Estimating the commutator* $[-\Delta,[-\Delta,|x|^3]$. We sketch the proof of positivy in Eq. (8). For a function, smooth enough so that the commutator $-[p^2,[p^2,f(x)]]$ is a least defined in the sense of quadratic form on $C_0^\infty(\mathbb{R}^3)$, we have the well-known identity

$$-[p^2,[p^2,f(x)]] = -(\Delta\Delta f)(x) + 4p\cdot(\mathrm{Hess} f(x))p.$$

Resorting to Hardy's trick, for a smooth real vector field $F:\mathbb{R}^3\to\mathbb{R}^3$, we can write

$$\begin{aligned} p\cdot\big(\mathrm{Hess}\, f(x)\big)\, p = &\big(p+iF(x)\big)\cdot\big(\mathrm{Hess}\, f(x)\big)\,\big(p-iF(x)\big)\\ &+ i\,\big(p\cdot\big(\mathrm{Hess}\, f(x)\big)F(x) - F(x)\cdot\big(\mathrm{Hess}\, f(x)\big)p\big)\\ &- F(x)\cdot\big(\mathrm{Hess}\, f(x)\big)F(x). \end{aligned}$$

For dimensional reasons (*i.e.* $p\cdot\psi$ should be homogeneous to $F(x)\psi$), it is natural to take $F(x)=\alpha x|x|^{-2}$ with $\alpha\in\mathbb{R}$. Moreover, let us restrict our study to radial functions, *i.e.* $f(x)=f(|x|)$. For convenient reasons, we denote $\omega_x = x/|x|$ and $r=|x|$. Tedious calculations show that

$$\begin{aligned} -\big[p^2\,,\,[p^2,f(|x|)]\big] =& 4\left(p+i\alpha\frac{\omega_x}{r}\right)\cdot\left((1-\omega_x\omega_x^T)\frac{f'(r)}{r}+\omega_x\omega_x^T f''(r)\right)\left(p-i\alpha\frac{\omega_x}{r}\right)\\ &- f^{(4)}(r) + 4\,(\alpha-1)\,\frac{f^{(3)}(r)}{r} + 4\alpha(1-\alpha)\frac{f''(r)}{r^2}. \quad (11) \end{aligned}$$

In particular, we have the following two lemmas:

Lemma 19. *Let $f:[0,\infty)\to\mathbb{R}$ be a convex non-decreasing function such that $x\mapsto f^{(4)}(|x|)\in L^1_{\mathrm{loc}}(\mathbb{R}^3)$. Then we have*

$$-\big[p^2\,,\,[p^2,f(|x|)]\big] \geqslant -f^{(4)}(|x|) \quad (12)$$

in the sense of quadratic forms on $C_0^\infty(\mathbb{R}^3)$.

Lemma 20 (Estimate on $-[p^2,[p^2,|x|^\beta]]$)**.** *For all $\beta\geqslant 1$, we have*

$$-\,[p^2,[p^2,|x|^\beta]] \;\geqslant\; \beta(\beta-1)(3-\beta)\,|x|^{\beta-4}, \quad (13)$$

in the sense of quadratic forms on $C_0^\infty(\mathbb{R}^3)$. In particular, positivy in Eq. (8) is proved.

Remark 12. We made a heavy used of the convexity of $x\mapsto|x|^\beta$ for $\beta\geqslant 1$ to get rid of the embarrassing Hessian term. By curiosity, we might try to give an explicit formula for $[-p^2,[p^2,|x|^3]]$. Luckily enough, one finds (after long tedious calculations) the rather compact formula

$$\frac{1}{12}[-p^2,[p^2,|x|^3]] = \frac{|x|(-\Delta)+(-\Delta)|x|}{2} - \nabla\cdot\frac{xx^T}{|x|}\nabla - \frac{1}{|x|}.$$

We then want to bound from below the elliptic operator $-\nabla \cdot \frac{xx^T}{|x|}\nabla$. For $\psi \in C_0^\infty(\mathbb{R}^3)$, one has

$$\left\langle \psi, -\nabla \cdot \frac{xx^T}{|x|}\nabla\psi \right\rangle = \int_{\mathbb{R}^3} \frac{|x \cdot \nabla\psi(x)|^2}{|x|}\mathrm{d}x.$$

By mimicking the proof of Hardy's inequality, one can prove that for all $\psi \in H^2(\mathbb{R}^d)$, we have

$$\frac{(d-1)^2}{4}\int_{\mathbb{R}^d} \frac{|u(x)|^2}{|x|}\mathrm{d}x \leqslant \int_{\mathbb{R}^d} \frac{|x \cdot \nabla u(x)|^2}{|x|}\mathrm{d}x.$$

Sadly enough, the constant $\frac{(d-1)^2}{4}$ being sharp, there is no hope in providing some function $g > 0$ such that $[-p^2, [p^2, |x|^3]] \geqslant g$ when $d = 3$.

3.1.3. *The proof.* Calculations made previously were mostly formal, since $[p^2, A_{|x|^3}]$ is *a priori* ill-defined. To fix this, consider the function $f_R(|x|) := R^3 f(|x|/R)$ where

$$f(r) = r - \arctan(r). \tag{14}$$

Therefore, f_R behave like $|x|^3$ on the ball $B(0,R) \subset \mathbb{R}^3$ and like $|x|$ at infinity. We have the following lemma:

Lemma 21. *Let f be as in Eq. (14). We have*

$$\frac{\big(f'(|x|)\omega_x - f'(|y|)\omega_y\big)\cdot(x-y)}{|x-y|^3} \geqslant \frac{1}{2}\frac{f'(|x|)}{|x|^2}\frac{f'(|y|)}{|y|^2} \tag{15}$$

for all $x \neq y \in \mathbb{R}^3$.

Let us now prove Theorem 18:

Proof of Theorem 18. Let $\psi \in H^2(\mathbb{R}^{3N})$ be an eigenvector of $H(N,Z)$ and f_R as previously defined. Let $\rho_\psi(\cdot) := \int_{\mathbb{R}^{3(N-1)}} |\psi(\cdot, x_2, \ldots, x_N)|^2 \mathrm{d}x_2 \ldots \mathrm{d}x_N$ the *electronic density* associated with ψ. We have

$$\begin{aligned}
0 =& \left\langle \psi, i\left(H(N,Z)\sum_{j=1}^N (A_{f_R})_{x_j} - \sum_{j=1}^N (A_{f_R})_{x_j} H(N,Z)\right)\psi \right\rangle \\
=& \sum_{j=1}^N \left\langle \psi, i[p_{x_j}^2, (A_{f_R})_{x_j}]]\psi \right\rangle - 2\sum_{j=1}^N \left\langle \psi, \nabla f_R(x_j)\cdot\nabla_{x_j}\left(-\frac{Z}{|x_j|} + \frac{1}{2}\sum_{k\neq j}\frac{1}{|x_j - x_k|}\right)\psi \right\rangle \\
>& -\frac{1}{R}\int_{\mathbb{R}^3} f^{(4)}\left(\frac{|x|}{R}\right)\rho_\psi(x)\,dx - 2Z\int_{\mathbb{R}^3}\frac{R^2 f'(|x|/R)}{|x|^2}\rho_\psi(x)\,dx \\
&+ \left\langle \psi, \left(\sum_{1\leqslant j\neq k\leqslant N} \frac{\big(\nabla f_R(x_j) - \nabla f_R(x_k)\big)\cdot(x_j - x_k)}{|x_j - x_k|^3}\right)\psi \right\rangle.
\end{aligned}$$

Using Eq. (15), we get

$$\begin{aligned}
&\left\langle \psi, \left(\sum_{1\leqslant j\neq k\leqslant N} \frac{(\nabla f_R(x_j) - \nabla f_R(x_k)) \cdot (x_j - x_k)}{|x_j - x_k|^3} \right) \psi \right\rangle \\
&\qquad \geqslant \frac{1}{2} \left\langle \psi, \left(\sum_{1\leqslant j\neq k\leqslant N} \frac{R^2 f_R'(|x_j|)}{|x_j|^2} \frac{R^2 f_R'(|x_k|)}{|x_k|^2} \right) \psi \right\rangle \\
&\qquad = \frac{1}{2} \left\langle \psi, \left(\sum_{j=1}^N \frac{R^2 f_R'(|x_j|)}{|x_j|^2} \right)^2 \psi \right\rangle - \frac{1}{2} \left\langle \psi, \left(\sum_{j=1}^N \left(\frac{R^2 f_R'(|x_j|)}{|x_j|^2} \right)^2 \right) \psi \right\rangle \\
&\qquad \geqslant \frac{1}{2} \left\langle \psi, \left(\sum_{j=1}^N \frac{R^2 f_R'(|x_j|)}{|x_j|^2} \right) \psi \right\rangle^2 - \frac{1}{2} \left\langle \psi, \left(\sum_{j=1}^N \frac{R^2 f_R'(|x_j|)}{|x_j|^2} \right) \psi \right\rangle \\
&\qquad = \frac{1}{2} \left(\int_{\mathbb{R}^3} \frac{R^2 f'(|x|/R)}{|x|^2} \rho_\psi(x)\, dx \right)^2 - \frac{1}{2} \int_{\mathbb{R}^3} \frac{R^2 f'(|x|/R)}{|x|^2} \rho_\psi(x)\, dx.
\end{aligned}$$

In the last line we have used Jensen's inequality as well as the fact that $f'(r)/r^2 = 1/(1+r^2) \leqslant 1$. Passing to the limit as $R \to \infty$ gives $N < 4Z + 1$. □

3.2. **Extension to the molecular setting.** We shall now extend the bound from the atomic setting to the molecular setting. Let us first define

$$F_R : \mathbb{R}^3 \ni x \mapsto \frac{1}{3} \sum_{j=1}^M f_R(x - R_j),$$

with f_R defined as previously, and suppose ψ is an eigenvector of $H(N)$. We follow the same strategy as in Theorem 18, replacing f_R by F_R and letting $R \to \infty$. As for the atomic case, the kinetic energy term γ_k is positive, and the interaction term γ_w is treated similarly from the fact that the estimate Eq. (15) is translation-invariant, *i.e.* letting $R \to \infty$, we have $-\gamma_w \geqslant \frac{1}{2} MN(N-1)$. Thus, we only need to bound γ_p. Explicit computations show that

$$\begin{aligned}
\gamma_p = \sum_{i=1}^N \left\langle \psi, \nabla F_R(x_i) \cdot \nabla_{x_i} \left(-\sum_{j=1}^M \frac{z_j}{|x_i - R_j|} \right) \psi \right\rangle &= \sum_{i=1}^M Z_i \int_{\mathbb{R}^3} \frac{\rho_\psi(x)}{1 + |x - R_i|^2/R^2} \mathrm{d}x \\
&+ \sum_{1\leqslant i\neq j\leqslant M} Z_j \int |x - R_i|(x - R_i) \cdot \frac{(x - R_j)}{|x - R_j|^3} \left[\frac{\rho_\psi(x)}{1 + |x - R_j|^2/R^2} \right] \mathrm{d}x.
\end{aligned}$$

By Cauchy-Schwarz, one has

$$|x - R_j|(x - R_j) \cdot \frac{x - R_k}{|x - R_k|^3} \leqslant 2 + \frac{2D^2}{|x - R_k|^2},$$

where $D := \max_{i<j} |R_i - R_j|$. Consequently, we have that

$$\gamma_p \leqslant NZ_{tot} + 2(M-1)Z_{tot}N + 2D^2(M-1) \sum_{k=1}^M Z_k \int_{\mathbb{R}^3} \frac{\rho_\psi(x)}{|x - R_k|^2} dx.$$

We are left to finding some estimate on $\int_{\mathbb{R}^3} \frac{\rho_\psi(x)}{|x-R|^2}dx$. Using Hardy's inequality and Hoffmann-Ostenhoff's inequality, one has

$$\int_{\mathbb{R}^3} \frac{\rho_{\psi(x)}}{|x-R|^2 dx} \leqslant 4 \int_{\mathbb{R}^3} \left| \nabla \sqrt{\rho_\psi(x)} \right|^2 dx \leqslant 4T_\psi,$$

where $T_\psi = \|\nabla\psi\|^2$ is the kinetic energy. But since $H(N)$ has no positive eigenvalues, we know for sure that $\mathcal{E}(\psi) \leqslant 0$, yielding

$$T_\psi \leqslant \sum_{j=1}^{M} \int_{\mathbb{R}^3} Z_j \frac{\rho_\psi(x)}{|x-R_j|} dx.$$

Since $|x-R|^{-1} \in L^{5/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$, cutting the singularity at R with a δ-ball and using Hölder's inequality, we have

$$\begin{aligned}\int_{\mathbb{R}^3} \frac{\rho_{\psi(x)}}{|x-R|} dx &\leqslant \delta^{-1}N + \int_{B(R,\delta)} \frac{\rho_{\psi(x)}}{|x-R|} dx \\ &\leqslant \delta^{-1}N + (4\pi\sqrt{\delta})^{2/5} \left(\int_{\mathbb{R}^3} \rho_\psi(x)^{5/3} dx \right)^{3/5}.\end{aligned}$$

The Hölder's exponents were carefully chosen so as to use the fundamental Lieb-Thirring inequality [25]. Indeed, we have that $\int_{\mathbb{R}^3} \rho_\psi(x)^{5/3} \mathrm{d}x \leqslant K^{-1}T_\psi$ with K a positive constant that verifies $K \geqslant (9/10)(2\pi)^{2/3}$ so that

$$\int_{\mathbb{R}^3} \frac{\rho_\psi(x)}{|x-R|} dx \leqslant \delta^{-1}N + (4\pi\sqrt{\delta})^{2/5} K^{-3/5} T_\psi^{3/5}.$$

Therefore, the kinetic energy T_ψ verifies the inequality

$$T_\psi \leqslant \delta^{-1} N Z_{tot} + \kappa(\delta) Z_{tot} T_\psi^{\frac{3}{5}} \qquad \text{with } \kappa(\delta) = \delta^{1/5} K^{-3/5} (4\pi)^{2/5}. \tag{16}$$

This means that $T_\psi \leqslant \sigma(N, Z_{tot})^5$ with $\sigma(N, Z_{tot}) := \inf_{\delta>0} R(N, Z_{tot}, \delta)$, where $R(N, Z_{tot}, \delta)$ is the first positive root of the polynomial $X^5 - \kappa(\delta) Z_{tot} X^3 - \delta^{-1} N Z_{tot}$. Therefore, putting pieces together, we have the inequality

$$N \leqslant 4\frac{Z_{tot}}{M} + 8\frac{M-1}{M} Z_{tot} + \frac{32D^2(M-1)Z_{tot}\sigma(N, Z_{tot})^5}{NM} + 1.$$

Solving for N yields the bound

$$\boxed{N \leqslant 4\left(2 - \frac{1}{M}\right) Z_{tot} + 1 + 4\sqrt{2} D Z_{tot}^{1/2} \sigma(N, Z_{tot})^{5/2}.}$$

Remark 13. This bound is rather inelegant (but willy-nilly, it's still a bound...), and disappointing for two reasons. The first is of course $\sigma(N, Z_{tot})$ not being even explicit. Numerical computations seems to show that $\sigma(N, Z_{tot}) = O(Z^{3/2})$, which is really bad for us. Secondly, though the appearance of D is not necessarily a bad in itself, this bound becomes quite cheap as the nuclei get far away for one another. Could we get rid of D by choosing another virial function ? To bound γ_w, convexity is a must (for γ_k as well, though we can get away, as in the last rem, by explicit computations). Therefore,

f *must* be chosen convex. Suppose we put $f(x) = \int |x - R| \mathrm{d}\mu(x)$ for some finite measure μ on $\mathbb{R}^3$. The term guilty for the appearance of D becomes

$$\sum_{i \neq j} Z_j \int_{\mathbb{R}^3} \mathrm{d}\mu(R) \int_{\mathbb{R}^3} |x - R|(x - R) \frac{(x - R')}{|x - R'|^3} \mathrm{d}x.$$

If we want this term to be bounded by some quantity independent of D, it must be independent by scaling. Therefore we should be getting a bound of the form $CZ_{tot}\|\rho_\psi\|_{L^1}$, which is impossible.

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