The quantum atomic model and the ionization conjecture

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Outline

Plan of the presentation :

- Quantum systems: Introduction and links with the Spectral Theory

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The single particle case

States of a 1 -particle system given by $\Psi \in \mathcal{H} = L^2(\mathbb{R}^3; \mathbb{C})$. The energy of the system is given by the Hamiltonian operator $H := -\Delta + V$:

$$\mathcal{E}(\Psi) := \langle \Psi, H\Psi \rangle = \int_{\mathbb{R}^d} p^2 |\hat{\Psi}(p)|^2 \, \mathrm{d}p + \int_{\mathbb{R}^d} V(x) |\Psi(x)|^2 \, \mathrm{d}x.$$

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Physical interpretation of $\mathcal{E}(\Psi)$:

- The term $-\langle \Psi, \Delta\Psi \rangle$ is the kinetic energy of the system.
- The map V is an external potential, which defines the potential part of the energy.

If V belongs to some suitable L^p spaces, the operator $-\Delta + V$ is self-adjoint over $H^1(\mathbb{R}^d)$.

Links with the Spectral Theory

Steady states of the system $\implies$ need to find the stationary states of the energy $\mathcal{E}(\Psi)$.

Recall: The wavefunction Ψ should live over the unit sphere, gradient of $\mathcal{E}(\Psi)$ collinear with Ψ:

$$\nabla\mathcal{E}(\Psi) = 2H\Psi = \lambda\Psi, \quad \lambda \in \mathbb{R}.$$

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So Ψ must be an eigenvalue of H, i.e the operator $(\lambda 1 - H)$ is invertible. Two possibilities:

- λ is in the *point spectrum* $\lambda \in \sigma_p(H)$.
- λ lies in the *approximate point spectrum*, so there exists a sequence x_n such that $\|(H-\lambda)x_n\| \to +\infty$.

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Definition (Discrete and essential spectrum)

We call *discrete spectrum* $\sigma_{disc}(H)$ the set of all $\in \sigma(H)$ isolated element of the point spectrum $\sigma_p(H)$ with finite multiplicity. The set $\sigma(H) \setminus \sigma_{disc}(H)$ is the *essential spectrum* $\sigma_{ess}(H)$.

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The essential spectrum is "stable" for small perturbations (the term $(A - i)^{-1}B$ must be compact) $\Longrightarrow$ under suitable condition over the potential V, we get information over the structure of $\sigma(H)$.

Essential spectrum of the Schroedinger operator

Proposition

Assume that $V \in L^p(\mathbb{R}^d) + L^\infty_\varepsilon(\mathbb{R}^d)$, *with p given by:*

$$\begin{cases} p = 1 & \text{if } d = 1 \\ p > 1 & \text{if } d = 2 \\ p = d/2 & \text{if } d > 2. \end{cases} \tag{1}$$

Then, we have:

$$\sigma_{ess}(-\Delta + V) = [0, +\infty).$$

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If V fulfills the conditions over the exponent p, then the term

$$v \in H^1(\mathbb{R}^d) \to \int_{\mathbb{R}^d} V(x)|v|^2 \,\mathrm{d}x$$

is weakly continuous with respect to the norm given by $H^1(\mathbb{R}^d)$.

Discrete spectrum of the Schroedinger operator

It remains to know what is the structure of the discrete spectrum of $H = -\Delta + V$. We define $\Sigma(-\Delta + V) := \min \sigma_{ess}(-\Delta + V)$, and $\mu_k(-\Delta + V)$ is the k-th eigenvalue of H.

Proposition

Assume that there holds the bound

$$V \leq -c|x|^{\alpha}, \quad 0 < \alpha < 2.$$

Then, the Schroedinger operator $-\Delta + V$ is such that:

$$\mu_k(-\Delta + V) < \Sigma(-\Delta + V) = 0, \quad \forall k \geq 1.$$

Therefore, the Hamiltonian operator has an infinite set sequence of negative eigenvalues, which converges to 0 as $k \to +\infty$.

First approach

Set of N electrons around 1 atomic nucleus in $\mathbb{R}^3 \implies$ behavior of the system given by the Hamiltonian:

$$H_{at}^N := -\sum_{j=1}^N \Delta_{x_j} - \sum_{j=1}^N \frac{z}{|x_j|} + \sum_{1\leq j<k\leq N} \frac{1}{|x_j - x_k|}$$

- States of the system given again by the eigenvectors of H_{at}^N.
- Solution to the equation $H_{at}^N \Psi_N = \lambda \Psi_N$ is such that

$$\Psi(x_1, ..., x_N) = \varepsilon(\sigma)\Psi(x_{\sigma(1)}, ..., x_{\sigma(N)}) \quad \forall \sigma \in \sigma_N, \qquad (2)$$

system of N interacting fermions.

Spectrum of H_{at}^N still splits in $\sigma_{ess}(H_{at}^N), \sigma_{disc}(H_{at}^N)$, but now the situation is more involved.

Spectrum of the atomic Hamiltonian (1)

Denote:

$$E_a^N := \min \sigma(H_{at}^N), \quad \Sigma_a^N := \min \sigma_{ess}(H_{at}^N).$$

Theorem (HVZ for atoms)

For the atomic Hamiltonian H_{at}^N, $E_a^N = 0$ and moreover:

$$\Sigma_a^N = E_a^{N-1}, \quad \forall N \geq 1.$$

- In the system with N fermions, the free state with the lowest energy is the $N-1$ bounded ground state.
- Proof relies on the tensorized product structure:

$$(H_{at}^N - \Sigma_a^N)\Psi \to 0 \implies \Psi(x_1, ..., x_N) = \Psi'(x_1, ..., x_{N-1})\varphi(x_N).$$

Spectrum of the atomic Hamiltonian (2)

Theorem (Discrete spectrum for H_{at}^N)

In $d = 3$ and with $z > 0$, H_{at}^N is such that:

- *If $N < z + 1$, H_{at}^N has an infinite set of eigenvalues under the essential spectrum:*

$$\mu_k(H_{at}^N) < \Sigma_a^N, \quad \forall k \in \mathbb{N}$$

- *If $N \geq z + 1$, H_{at}^N has a finite number of eigenvalues under the essential spectrum, hence for k large enough:*

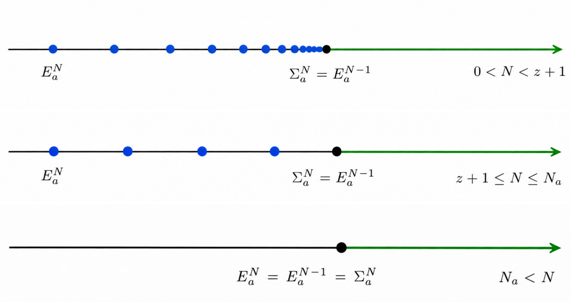
$$\mu_k(H_{at}^N) = \Sigma_a^N.$$

- *There exists a number N_a such that for every $N > N_a$ there holds:*

$$E_a^N = E_a^{N-1} = \Sigma_a^N.$$

Comments

- Graphically the situation is the following:



- Similar result holds for molecules. In this case the relevant constant is

$$Z := \sum_{m=1}^{M} z_m,$$

where M is the total number of atomic nuclei.

Estimating N_a

We know that if $N > N_a \implies$ the atom is "ionized"

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Can we give an estimate for the value of N_a?

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In nature the maximum negative charge for ions is not too high, so we expect to have a bound of the following type:

$$N_a < Z + C,$$

where Z is the total charge of the nucleus, and C is a constant.

Theorem (Lieb,'84)

We have:

$$N_a < 2Z + 1.$$

Lieb's estimate shows ionization conjecture up to a factor 2.

Proof of Lieb's bound (1)

Proof: Starting from the equation $(H_{at}^N - E_a^N)\Psi_N = 0$, multiply by $x_N\bar{\Psi}_N$ and integrate, getting:

$$\langle |x_N|\Psi_N, (H_{at}^N - E_a^N)\Psi_N\rangle = 0 \tag{3}$$

We can rewrite this as:

$$(3) = \langle |x_N|\Psi_N, (H_{at}^{N-1} - E_a^N)\Psi_N\rangle + \frac{1}{2}\langle |x_N|\Psi_N, -\Delta_N\Psi_N\rangle$$
$$+ \left\langle \Psi_N, \left[-Z + \sum_{i=1}^{N-1}\frac{|x_N|}{|x_i - x_N|}\right]\Psi_N \right\rangle.$$

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$$+ \left\langle \Psi_N, \left[-Z + \sum_{i=1}^{N-1} \frac{|x_N|}{|x_i - x_N|}\right] \Psi_N \right\rangle.$$

The first term is non negative, because of the definition of E_a^N and E_a^{N-1}. For the second one:

$$\mathrm{Re}(\langle |x|f, -\Delta f\rangle) \geq 0, \quad \forall f \in H^1(\mathbb{R}^3).$$

Hence, the third term must be negative.

Proof of Lieb's bound (2)

Now, denote with $S_{N-1} = \sum_{i=1}^{N-1} \frac{|x_N|}{|x_i - x_N|}$ and use the symmetry property of fermionic wavefunctions:

$$\langle \Psi_N, (-Z + S_{N-1})\Psi_N \rangle = \left\langle \Psi_N, \left[-Z + \frac{1}{N} \sum_{1 \leq j \leq i \leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|} \right] \Psi_N \right\rangle$$

$$\leq 0.$$

From the triangle inequality, we have that:

$$\frac{1}{N(N-1)} \sum_{1 \leq j \leq i \leq N} \frac{|x_i| + |x_j|}{|x_i - x_j|} \geq \frac{1}{N(N-1)} \sum_{i=1}^{N} i = \frac{1}{2}.$$

And so, this tells us that $-ZN + \frac{N(N-1)}{2} < 0$, and this gives us the claim.

Thanks for the attention!

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