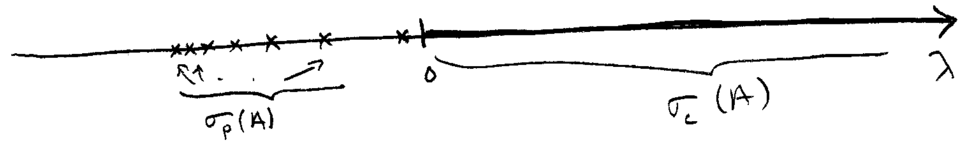


Our calculations indicate that the spectrum of $A = -\partial_{xx} + V(x)$ (for the V chosen above) is equal to the union of a finite number of eigenvalues and $[0, \infty)$:

$$\sigma(A) = \{\lambda_i\}_{i=1}^{N} \cup [0, \infty),$$

where the eigenvalues $\lambda_i < 0$ are given by

$$\lambda_i = \rho_i^2 - M < 0,$$

where ρ_i satisfies ✡, and the continuous spectrum of A is $[0, \infty)$.

There is a theorem that tells us that in fact, in this case, the continuous spectrum of $-\partial_{xx} + V$ is the same as that of $-\partial_{xx}$.

Defn The discrete spectrum $\sigma_d(T)$ of an operator T in $\mathcal{H}$ is the set of all eigenvalues λ of T ($\lambda \in \sigma_p(T)$) such that $\dim(\mathrm{Null}(\lambda I - T)) < \infty$ and λ is isolated in $\sigma(T)$.

The essential spectrum $\sigma_{ess}(T)$ of T is the complement of $\sigma_d(T)$ in $\sigma(T)$: $\sigma_{ess}(T) = \sigma(T) - \sigma_d(T)$.

A good reference for this is Hislop/Sigal, Introduction to Spectral Theory with Applications to Schrödinger Operators, Ch. 14.

Defn Let A be a closed operator with $\rho(A) \neq \phi$. An operator B is called relatively A-compact (or compact relative to A) if

(i) $\mathcal{D}(A) \subset \mathcal{D}(B)$,

(ii) $B|_{\mathcal{D}(A)} : \mathcal{D}(A) \to \mathcal{H}$ is compact when $\mathcal{D}(A)$ is endowed with the graph norm of A.

Recall that the graph norm of A is given by

$$\|v\|_A = \|v\| + \|Av\|, \quad v \in \mathcal{D}(A).$$

Condition (ii) is equivalent to the condition

(ii') $B(\lambda I - A)^{-1} : \mathcal{H} \to \mathcal{H}$ is compact for all $z \in \rho(A)$.

<u>Theorem</u> Let T and V be self-adjoint operators in $\mathcal{H}$ with V relatively T-compact. Then $T+V$ is self adjoint in $\mathcal{H}$ (with $\mathcal{D}(T+V) = \mathcal{D}(T)$) and

$$\sigma_{ess}(T+V) = \sigma_{ess}(T).$$

$\star\to$ In the theory of expansions in generalized eigenfunctions, one learns that an arbitrary L^2-function is given uniquely by a linear combination of eigenfunctions of $-\Delta + V$ plus an integral superposition of extended states of $-\Delta + V$.

The Hydrogen atom

Usually, one uses $\frac{1}{|x|}$ rather than $\frac{2}{|x|}$

Let us now turn to the Schrödinger operator in $\mathbb{R}^3$.
We will omit the constant multiplying Δ and simply write

$$h = -\Delta - \frac{2}{|x|} \quad , \quad \mathcal{D}(h) = H^2(\mathbb{R}^3) \subset L^2(\mathbb{R}^3, dx)$$

where $x \in \mathbb{R}^3$ and $|x| = \left(\sum_{i=1}^{3} x_i^2\right)^{1/2}$.

The material may be found in Reed/Simon XIII.6 or in Gustafson/Sigal §7.7 or Hislop/Sigal.

The spectrum of h

Through the Fourier transform, one finds that the spectrum of $-\Delta$ is $[0,\infty)$. In fact

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

This is seen, as in the 1D case, by considering the unitarily equivalent operator $-\hat{\Delta} = T_{\omega^2}$ in $L^2(\mathbb{R}^3, d\omega)$.

It can also be shown that the operator of multiplication by $-2/|x|$ is compact relative to Δ. Therefore, by the previous theorem,

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

In fact, it can be shown that

$$\sigma_p(h) = \left\{ \frac{-1}{j^2} \right\}_{j=1}^{\infty}$$

In quantum mechanics, the eigenfunctions ϕ_n, satisfying

$$\left(-\Delta - \frac{2}{|x|}\right)\phi_j(x) = -\frac{1}{j^2}\phi_j(x), \quad \|\phi_j(x)\|_{L^2} = 1$$

are the "bound states". The interpretation is that $|\phi_j(x)|^2$ is the probability distribution for the position of an electron at energy level $-\frac{1}{j^2}$. This distribution is concentrated around $x=0$, where a fixed proton is giving rise to the Coulomb potential

$$V(x) = -\frac{2}{|x|}.$$

[Remember that this problem is nondimensionalized here.]

The extended states, or scattering states, can be constructed as in our 1D toy model for $\lambda \in [0,\infty)$:

$$\left(-\Delta - \frac{2}{|x|} - \lambda\right) f_n^\lambda(x) \to 0 \qquad (n\to\infty)$$

These are interpreted as steady-state wave forms arising upon illuminating the proton with a plane wave emanating from infinity forever [So they are idealized].

The eigenvalues of $-\Delta - \frac{2}{|x|}$ are equal to the quanta of energy that a Hydrogen atom can take on — these are associated with the orbits studied in physical chemistry.

Kwik-notes on … The Helium atom (Reed/Simon § XII.6, Vol. IV)

We will take an intuitive and heuristic approach.

The Helium atom is modeled by a Hamiltonian in $L^2(\mathbb{R}^6)$:

$$H = -\Delta_x - \frac{2}{|x|} - \Delta_y - \frac{2}{|y|} + \frac{1}{|x-y|},$$

where $x \in \mathbb{R}^3$ and $y \in \mathbb{R}^3$, Δ_x is the Laplacian in $L^2(\mathbb{R}^3, dx)$ and Δ_y is the Laplacian in $L^2(\mathbb{R}^3, dy)$. We begin by considering the operator

$$H_0 = -\Delta_x - \frac{2}{|x|} - \Delta_y - \frac{2}{|y|},$$

which we may call the "unperturbed" operator.

Functions in $L^2(\mathbb{R}^6)$ are interpreted as giving a joint probability distribution for the positions of two electrons (when normalized). The term $1/|x-y|$ models the Coulomb interaction between the two electrons, which is ignored in H_0.

We proceed to find eigenfunctions of H_0, allowing them to be general functions (not necessarily in $L^2(\mathbb{R}^6)$). Since H_0 is the sum of two operators, one on $L^2(\mathbb{R}^3, dx)$ and one on $L^2(\mathbb{R}^3, dy)$, eigenfunctions can be found by considering the separable form

$$\psi(x,y) = \psi_1(x)\,\psi_2(y).$$

It can be shown that all eigenfunctions of H_0 are separable.

Let $\psi(x,y) = \psi_1(x)\psi_2(y)$ be an eigenfunction of H_0 with eigenvalue λ:

$$(H_0 - \lambda)\psi(x,y) = 0, \qquad \text{or}$$

$$\underbrace{\left[\left(-\Delta_x - \frac{1}{|x|}\right)\psi_1(x)\right]}_{\text{fcn of } x}\underbrace{\psi_2(y)}_{\text{fcn of } y} + \underbrace{\left[\left(-\Delta_y - \frac{1}{|y|} - \lambda\right)\psi_2(y)\right]}_{\text{fcn of } y}\underbrace{\psi_1(x)}_{\text{fcn of } x} = 0$$

Since this equality holds for each (x,y), we obtain

$$\left.\begin{aligned} \left(-\Delta_x - \frac{1}{|x|}\right)\psi_1(x) &= \lambda_1\psi_1(x) \\ \left(-\Delta_y - \frac{1}{|y|} - \lambda\right)\psi_2(y) &= -\lambda_1\psi_2(y) \end{aligned}\right\} \text{ for some } \lambda_1,$$

and we obtain two separate eigenvalue problems

$$\left.\begin{aligned} \left(-\Delta_x - \frac{1}{|x|}\right)\psi_1(x) &= \lambda_1\psi_1(x) \\ \left(-\Delta_y - \frac{1}{|y|}\right)\psi_2(y) &= \lambda_2\psi_2(x) \end{aligned}\right\} \lambda_1 + \lambda_2 = \lambda.$$

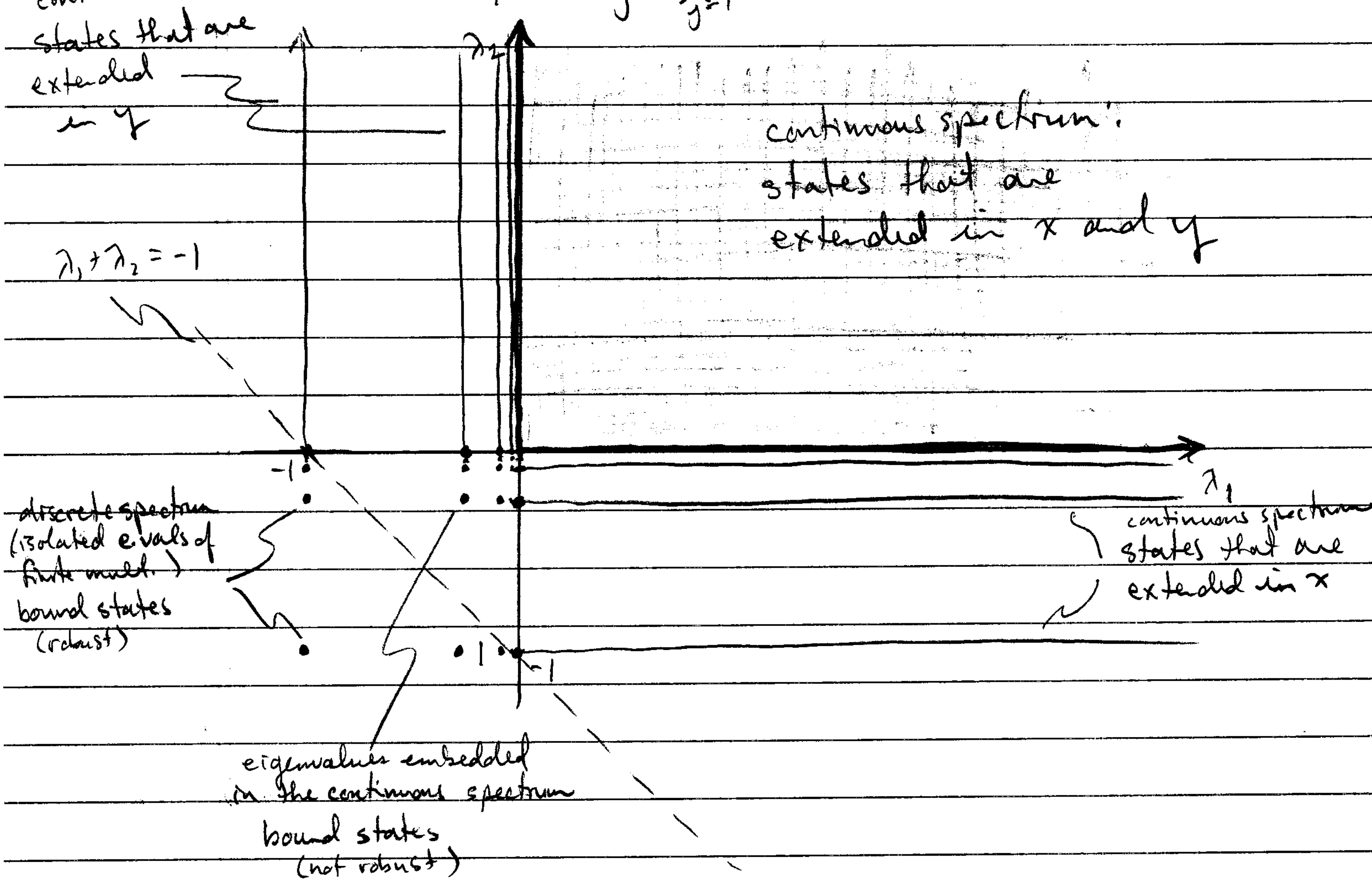
This heuristic leads to the conjecture (which can be proved) that the spectral values of H_0 are obtained as sums of spectral values of $-\Delta_x - \frac{1}{|x|}$ and $-\Delta_y - \frac{1}{|y|}$ and that the corresponding eigenfunctions are products of eigenfunctions of the individual operators:

$$\left\{\begin{array}{l} \sigma(H_0) = \left\{\lambda_1 + \lambda_2 : \lambda_1, \lambda_2 \in \sigma\left(-\Delta - \frac{1}{r}\right)\right\} \\[1em] \text{For } \lambda \in \sigma(H_0), \text{ the (generalized) eigenfunctions are} \\ \quad \psi(x,y) = \psi_1(x)\psi_2(y) \text{ where } \left(-\Delta - \frac{1}{r}\right)\psi_1 = \lambda_1\psi_1 \\ \qquad\qquad\qquad\qquad\qquad\qquad \left(-\Delta - \frac{1}{r}\right)\psi_2 = \lambda_2\psi_2, \ \lambda_1 + \lambda_2 = \lambda. \end{array}\right.$$

Thus we obtain the spectrum of H_0:

$$\sigma(H_0) = \left\{ \lambda_1 + \lambda_2 : \lambda_1, \lambda_2 \in [0,\infty) \cup \left\{ \frac{1}{-j^2} \right\}_{j=1}^{\infty} \right\}$$

$$= \left\{ -1 - \frac{1}{j^2} \right\}_{j=1}^{\infty} \cup [-1, \infty)$$



Bound states : $\psi(x,y) = \psi_1(x)\psi_2(y)$, where both ψ_1 or ψ_2 are eigenfunctions of $-\Delta - \frac{1}{r}$.
$\in L^2$ $\in L^2$ Isolated if ψ_1 or ψ_2 has e.val -1.

Extended states : $\psi(x,y) = \psi_1(x)\psi_2(y)$, where either (or both of) ψ_1 or ψ_2 is an extended state of $-\Delta - \frac{1}{r}$.

Now lets consider H, or, more generally, a family of operators

$$H_\beta = H_0 + \beta V,$$

where $V = \frac{1}{|x-y|}$.

By a theorem of Kato and Rellich (Reed/Simon Thms XII.8, 13, Vol. IV), each element of the discrete spectrum $\{-1-\frac{1}{j^2}\}_{j=1}^{n}$ splits into m isolated eigenvalues of H_β for β small enough, where m is the multiplicity of the eigenvalue of H_0.

Thus, we see that the discrete spectrum, counted according to multiplicity, is robust under (small) perturbations of β.

However, embedded eigenvalues typically "dissolve into the continuous spectrum" and are therefore nonrobust under perturbations. This is known as "autoionization" in physical chemistry. The idea is that an eigenvalue of H_0, say $\lambda = -1/2$ (corresponding to $\lambda_1 = -1/4$ and $\lambda_2 = -1/4$ with bound state $\psi_1(x)\psi_2(y)$) ceases to exist when $\beta \neq 0$. The state morphs into a state that is extended in the x- or y- direction, i.e., one of the electrons escapes to infinity and the atom becomes an ion.

This autoionization is related to anomalous scattering ($0<\beta<<1$) near the frequency of the embedded eigenvalue (at $\beta=0$). [See diagrams in Reed/Simon.]