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

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

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

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

where $E_i$ satisfies $\Delta$, 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 $-\Delta x + V$ is the same as that of $-\Delta x$.

Define the discrete spectrum $\sigma_d(T)$ of an operator $T$ in $\mathcal{H}$ is the set of all eigenvalues $\lambda$ of $T$ ($\lambda \in \sigma_1(T)$) such that $\dim(\text{Null}(T - \lambda I)) < \infty$ and $\lambda$ 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's Introduction to Spectral Theory with Applications to Schrödinger Operators, Ch. 14.
Let $A$ be a closed operator with $\rho(A) \neq \emptyset$. An operator $B$ is called relatively $A$-compact (or compact relative to $A$) if

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

(ii) $B|_{\mathcal{D}(A)} : \mathcal{D}(A) \rightarrow \mathcal{H}$ 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

(iii) $B(\lambda I - A)^{-1} : \mathcal{H} \rightarrow \mathcal{H}$ is compact for all $\lambda \in \rho(A)$.

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

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

\

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

Let us now turn to the Schrödinger operator in $\mathbb{R}^3$.

We will omit the constant multiplying $A$ and simply write

\[
\mathcal{H} = -\mathcal{A} - \frac{2}{|x|}, \quad \mathcal{D}(\mathcal{H}) = L^2(\mathbb{R}^3, dx)
\]

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 XII.10 or in Gustafson/Sigal §7.7 or Hislop/Sigal.

The spectrum of \( \mathcal{H} \)

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

\[
\sigma(-\mathcal{A}) = \sigma_c(-\mathcal{A}) = \sigma_{ess}(-\mathcal{A}) = [0, \infty).
\]

This is seen as in the 1D case, by considering the unitarily equivalent operator $-\hat{\mathcal{A}} = \int_0^\infty \chi \leq L^2(\mathbb{R}^3, dx)$.

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

\[
\sigma_{ess}(\mathcal{H}) = \sigma_{ess}(-\mathcal{A}) = [0, \infty).
\]

In fact, it can be shown that

\[
\sigma_p(\mathcal{H}) = \left\{ \frac{1}{j^2} \right\}_{j=1}^{\infty}
\]
In quantum mechanics, the eigenfunctions $\phi_n$, satisfying

$$(-\Delta - \frac{2}{|x|}) \phi_n(x) = \frac{1}{j^2} \phi_n(x), \quad \| \phi_n(x) \|_2^2 = 1$$

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 non-dimensionalized here.]

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

$$(-\Delta - \frac{2}{|x|} - \lambda) \phi_n(x) \to 0 \quad (n \to \infty)$$

These are interpreted as steady-state wave forms arising after 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 quantum of energy that a Hydrogen atom can take on — these are associated with the orbits studied in physical chemistry.
We will take an intuitive and heuristic approach.

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

$$H = -\Delta_x - \frac{2}{|x|} - 4\Delta_y - \frac{2}{|y|} + \frac{1}{|x-y|}$$

where $x \in \mathbb{R}^3$ and $y \in \mathbb{R}^3$, $\Delta_x$ is the Laplacian in $L^2(\mathbb{R}^3, dx)$ and $\Delta_y$ is the Laplacian in $L^2(\mathbb{R}^3, dy)$.

We begin by considering the operator

$$H_0 = -\Delta_x - \frac{2}{|x|} - 4\Delta_y - \frac{2}{|y|}$$

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 $\frac{1}{|x-y|}$ 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 formed by considering the separable form

$$\psi(x,y) = \Phi_1(x) \Phi_2(y)$$

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 \( \lambda \) : 

\[
(H_0 - \lambda) \psi(x, y) = 0,
\]

or

\[
\left[ (-4x - \frac{1}{|x|}) \psi_1(x) \right] \frac{\psi_1(x)}{\text{fn of } x} + \left[ (-4y - \frac{1}{|y|} - \lambda) \psi_2(y) \right] \frac{\psi_2(y)}{\text{fn of } y} = 0
\]

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

\[
\begin{align*}
(-4x - \frac{1}{|x|}) \psi_1(x) &= \lambda \psi_1(x) \\
(-4y - \frac{1}{|y|} - \lambda) \psi_2(y) &= -\lambda \psi_2(y)
\end{align*}
\]

and we obtain two separate eigenvalue problems

\[
\begin{align*}
(-4x - \frac{1}{|x|}) \psi_1(x) &= \lambda \psi_1(x) \\
(-4y - \frac{1}{|y|}) \psi_2(y) &= \lambda \psi_2(y)
\end{align*}
\]

This heuristic leads to the conjecture (which can be proved) that the spectral values of \( H_0 \) are obtained as sums of spectral value of \(-4x - \frac{1}{|x|}\) and \(-4y - \frac{1}{|y|}\) and that the corresponding eigenfunctions are products of eigenfunctions of the individual operators:

\[
\sigma(H_0) = \{ \lambda_1 + \lambda_2 : \lambda_1, \lambda_2 \in \sigma(-4 - \frac{1}{|x|}) \}
\]

For \( \lambda \in \sigma(H_0) \), the (generalized) eigenfunctions are

\[
\psi(x, y) = \psi_1(x) \psi_2(y) \text{ where } (-4 - \frac{1}{|x|}) \psi_1 = \lambda \psi_1,
\]

\[
(-4 - \frac{1}{|y|}) \psi_2 = \lambda \psi_2 \text{ and } \lambda_1 + \lambda_2 = \lambda.
\]
Thus we obtain the spectrum of $H_0$:

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

**Continuous spectrum:**

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

**States that are extended in $x$ and $y$**

**Discrete spectrum (isolated energy levels of finite model)**

**Bound states (robust)**

**Eigenvalues embedded in the continuous spectrum**

**Bound states (not robust)**

**Continuous spectrum**

**States that are extended in $x$**

**Extended states:** $\psi(x,y) = \psi_1(x) \psi_2(y)$, where either

- $\psi_1$ or $\psi_2$ are eigenfunctions of $-\Delta - \frac{1}{4}$
- $\psi_1^2 + \psi_2^2$ is isolated if $\psi_1$ or $\psi_2$ has level 1.

**Extended states:** $\psi(x,y) = \psi_1(x) \psi_2(y)$, where one (or both) of

- $\psi_1$ or $\psi_2$ is an extended state of $-\Delta - \frac{1}{4}$. 
Now let's consider $H_p$ or, more generally, a family of operators

$$H_p = H_0 + pV,$$

where $V = \frac{1}{|x-y|^2}$.

By a theorem of Kato and Rellich (Reed/Simon Thm. XII.3, Vol. III), each element of the discrete spectrum $\mathcal{S}$ of $H_p$, $\lambda - \frac{1}{2} \sum \delta_{\gamma}$, splits into $m$ isolated eigenvalues of $H_p$ for $p$ 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 $p$.

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 $\gamma = -\frac{1}{2}$ and $\gamma = -\frac{1}{2}$ with bound state $\psi(x,y)$), ceases to exist when $p \neq 0$. 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 ($0 < p \ll 1$) near the frequency of the embedded eigenvalue ($\lambda = 0$). [See diagrams in Reed/Simon.]