CONVERGENCE OF THE GROUND STATE ENERGY OF HELIUM ATOM

MATTEO MOESSNER

Abstract. In classical quantum mechanics, Hamiltonian operators must be self-adjoint to obtain a physically meaningful energy level. Although the hydrogen atom Hamiltonian admits an exact self-adjoint formulation, verifying this property for the helium atom Hamiltonian is much less trivial. Furthermore, the convergence of helium ground state energy series is not easily determined. In this work, we analyze the reduced form of the Hamiltonian, the Schrödinger operator, and apply analytic perturbation theory for unbounded operators to estimate the radius of convergence for the ground state energy series of the helium Schrödinger operator. We provide 3 derivations for the lower bound, the last of which provides a valid expansion for the helium $Z = 2$ case.

Contents

Date: August 28, 2025.

1. Theory of Unbounded Operators

For the duration of this paper, we will be working with *Hilbert spaces*. That is, a complex Banach space whose norm is induced by an inner product. We begin by discussing *unbounded operators* in a separable Hilbert space, which we denote as $\mathcal{H}$ throughout the paper. An unbounded operator T is different from bounded operators in that an unbounded operator T is a linear mapping defined on a linear subspace $\mathcal{D}(T) \subset \mathcal{H}$, called the *domain* of T, and takes value in $\mathcal{H}$. Unless otherwise stated, we will always use the operator norm

$$\|T\| := \sup_{\|u\|=1} \|Tu\|, \quad u \in \mathcal{H}. \tag{1.1}$$

However, unbounded operators do not necessarily have finite operator norm.

In this section, we introduce the basic definitions and theorems that are useful for the theory of unbounded operators. Throughout this paper, the standard, well-established results from [6] will be stated without proof. We refer the reader to the text if they are interested in the proof.

1.1. Adjoint Operators.

The definitions and theorems in this subsection are directly cited from Section III §§5.1, 5.2, 5.3, and 5.5 of [6]. Henceforth, we only consider *densely defined* operators, namely $\mathcal{D}(T)$ is dense within $\mathcal{H}$.

Definition 1.2. Let $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ be a densely defined operator. The *graph* of T is the linear subspace

$$\mathcal{G}(T) := \{(x, Tx) : x \in \mathcal{D}(T)\} \subset \mathcal{H} \times \mathcal{H}.$$

The operator T is said to be a *closed* operator, if $\mathcal{G}(T)$ is a closed linear subspace of $\mathcal{H} \times \mathcal{H}$. The operator T is *closeable* if the closure of $\mathcal{G}(T)$ is itself the graph of some operator $\overline{T}$.

Equivalently, T is closed if for any Cauchy sequence $\{u_n\}_{n\in\mathbb{N}} \subset \mathcal{D}(T)$,

$$\lim_{n\to\infty} u_n = u \text{ and } \lim_{n\to\infty} Tu_n = v \quad \text{implies} \quad u \in \mathcal{D}(T) \text{ and } Tu = v.$$

Throughout this paper, we use $u_n \to u$ to denote convergence in the Hilbert space norm. Therefore, T is closeable if and only if for any Cauchy sequence $\{u_n\}_{n\in\mathbb{N}} \in \mathcal{D}(T)$,

$$u_n \to 0 \text{ and } Tu_n \to v \quad \text{implies} \quad v = 0. \tag{1.3}$$

We call $\overline{T}$ the closure of T. Formally, it is the smallest closed extension of T.

The definition of the adjoint for an unbounded operator is slightly more involved than that for bounded ones. Specifically, it only makes sense for densely defined operators.

Theorem 1.4. *Let $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ be a densely defined operator. Then, for each $v \in \mathcal{H}$ there exists $z \in \mathcal{H}$ such that*

$$\langle Tu, v\rangle = \langle u, z\rangle \quad \textit{for all} \quad u \in \mathcal{H}. \tag{1.5}$$

Defining $T^*v = z$, we obtain an operator $T^* : \mathcal{D}(T^*) \subset \mathcal{H} \mapsto \mathcal{H}$, called the adjoint of T.

We will be particularly concerned with the case of symmetric adjoint operators.

Definition 1.6. A densely defined operator $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ is called *symmetric*, or *Hermitian* when we only consider complex Hilbert spaces, if $\mathcal{D}(T) \subseteq \mathcal{D}(T^*)$, and $Tu = T^*u$ for all $u \in \mathcal{D}(T)$. Equivalently, T is symmetric if $\mathcal{D}(T) \subseteq \mathcal{D}(T^*)$, and for all $u, v \in \mathcal{D}(T)$,

$$\langle Tu, v\rangle = \langle u, Tv\rangle. \tag{1.7}$$

It is important to mention that if an operator T is densely defined, then its adjoint is a closed operator. Using this fact and the definition of being symmetric, we can actually ascertain that symmetric operators are closeable.

Theorem 1.8. *If T is a symmetric operator, then it is closeable.*

Proof. By definition of symmetry, for all $u \in \mathcal{D}(A), v \in \mathcal{D}(A^*)$, we have

$$\langle Au, v\rangle = \langle u, Av\rangle = \langle u, A^*v\rangle, \quad \text{which implies} \quad \langle Au, v\rangle - \langle u, A^*v\rangle = 0. \tag{1.9}$$

Thus, $\mathcal{G}(-T^*)$ annihilates $\mathcal{G}(T)$. In other words,

$$\mathcal{G}(-T^*) = \mathcal{G}(T)^\perp$$

where $\mathcal{G}(T)^\perp$ is a closed subset of $\mathcal{H} \times \mathcal{H}$. Because T^* is also densely defined (to be justified shortly), taking the orthogonal complement once again gives

$$G(T^{**}) = \left(\mathcal{G}(T)^\perp\right)^\perp,$$

where $G(T^**)$ is also closed. However, in a Hilbert space the orthogonal complement of the orthogonal complement of a set is the original set's closure, meaning $G(T^**) = \overline{\mathcal{G}(T)}$ as required.

The rest of this proof will be dedicated to proving that T^* is densely defined. We first assume that it is not dense. A linear subspace in $\mathcal{H}$ is dense if and only if its orthogonal complement is trivial, so we can assume there exists some nonzero $v \in \mathcal{H}$ such that

$$\langle v, u\rangle = 0 \quad \text{for all} \quad u \in D(T^*). \tag{1.10}$$

This implies $(v, 0) \in \left(\mathcal{G}(T)^\perp\right)^\perp = \overline{\mathcal{G}(T)}$. Therefore, T is closeable with closure $\overline{T}$. By the definition of closeability, there exists some Cauchy sequence $\{x_n\}_{n\in\mathbb{N}} \in \mathcal{D}(T)$ such that

$$\lim_{n\to\infty} x_n = 0, \quad \lim_{n\to\infty} Tx_n = v.$$

By closeability, it is necessarily true that $v = \{0\}$. This implies that the orthogonal complement of $D(T^*)$ is $\{0\}$, which implies that $D(T^*)$ is dense as required. □

We now recall the definition of an unbounded self-adjoint operator.

Definition 1.11. A densely defined operator $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ is called *self-adjoint* if $\mathcal{D}(T) = \mathcal{D}(T^*)$ and T is symmetric. In other words,

$$T = T^*. \tag{1.12}$$

1.2. **Relative Boundedness.** Although an unbounded operator may not admit a finite norm, one can still define boundedness at least on the domain of some other operator. These definitions and theorems are directly cited from sections IV §§1.1 and 1.3 of [6].

Definition 1.13. Let T and A be densely defined operators on $\mathcal{H}$ with $\mathcal{D}(A) \supset \mathcal{D}(T)$. We say that A is *relatively bounded with respect to T* or is *T-bounded*, if for some $a, b \geq 0$,

$$\|Au\| \leq a\|u\| + b\|Tu\|, \quad \text{for all } u \in \mathcal{D}(T). \tag{1.14}$$

We call the infimum of b that satisfies this bound, b_0, the *T-bound* of A.

Relative boundedness can be extended to other operators.

Corollary 1.15. *Take T and A as (1.14) with T-bound $b < 1$ and define $S = T + A$. Assume further there exists a densely defined operator A' such that (1.14) holds for some $b = \beta$. Then for $u \in \mathcal{D}(T)$, A' is S-bounded with S-bound $\beta(1-b)^{-1}$.*

Proof. From (1.14) and the definition $S = T + A$,

$$\|Au\| \leq a\|u\| + b\|Tu\| = a\|u\| + b\|(S - A)u\|.$$

Since $b < 1$, rearranging gives

$$\|Au\| \leq \frac{1}{1-b}\big(a\|u\| + b\|Su\|\big). \tag{1.16}$$

By assumption on A',

$$\|A'u\| \leq a\|u\| + \beta\|Tu\| = a\|u\| + \beta\|(S - A)u\|.$$

Applying (1.16) to control $\|Au\|$, we obtain

$$\|A'u\| \leq a\left(1 + \frac{\beta}{1-b}\right)\|u\| + \frac{\beta}{1-b}\|Su\|.$$

A' is then S-bounded with S-bound $\frac{\beta}{1-b}$. □

Definition 1.17. Let $T, A : X \to Y$ be operators where $\mathcal{D}(A) \supset \mathcal{D}(T)$. Let $u_n \in D(T)$ be a Cauchy sequence. If $\{u_n\}, \{Tu_n\}$ are bounded and $\{Au_n\}$ has a convergent subsequence, then A is *relatively compact with respect to T* or *T-compact*.

If A is T-compact then it is also T-bounded.

We are at the place to introduce one of the most important results in the theory of unbounded operators which we cite from [9].

Theorem 1.18 (Kato-Rellich Theorem I)**.** *Let $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ be self-adjoint and A be T-bounded with $b < 1$. Then, $T + A : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ is still self-adjoint.*

1.3. **Sesquilinear Forms.** The tools we have developed thus far are enough for a discussion on unbounded operators. However, it is generally difficult to extrapolate any information from them. As we will see shortly, it is far easier to deal with operators when associating them with a form. These definitions and theorems are directly cited from sections VI §§1.1-4, 1.7, 2.1, and 2.3 of [6].

Let $\mathcal{H}$ be a Hilbert space as before. A *sesquilinear form* is a function $\mathfrak{t} : \mathcal{D}(\mathfrak{t}) \times \mathcal{D}(\mathfrak{t}) \mapsto \mathbb{C}$ defined on a dense subspace $\mathcal{D}(\mathfrak{t}) \subset \mathcal{H}$, which is linear in the 2nd argument and conjugate linear in the 1st argument. A sesquilinear form $\mathfrak{t}$ is called symmetric or *Hermitian* if for $u, v \in \mathcal{D}(\mathfrak{t})$,

$$\mathfrak{t}(u, v) = \overline{\mathfrak{t}(v, u)}.$$

We shall see later that a Hermitian sesquilinear form will naturally give rise to self-adjoint operators under some mild conditions. Therefore, we will exclusively work with Hermitian forms.

We also define $\mathfrak{t}[u] = \mathfrak{t}(u,u)$ to be the *quadratic form* related to $\mathfrak{t}$. Specifically, when $\mathfrak{t}$ is Hermitian, the quadratic form $\mathfrak{t}[u]$ is real-valued. Associated to quadratic forms is the notion of coercivity.

Definition 1.19. A symmetric form $\mathfrak{t}$ is said to be *coercive* if the set of (real) values $\mathfrak{t}[u]$ for $\|u\| = 1$ is bounded from below:

$$\mathfrak{t}[u] \geq \gamma \|u\|^2, \quad u \in \mathcal{D}(\mathfrak{t})$$

for $\gamma \in \mathbb{R}$. The supremum of γ that satisfy this bound, γ_0 is called the *lower bound* of $\mathfrak{t}$. If $\gamma_0 \geq 0$, $\mathfrak{t}$ is called non-negative.

The quadratic form also lets us use the graph norm on $\mathfrak{t}[u]$.

$$\|u\|_{\mathfrak{t}} := \|u\|_{\mathcal{H}} + \mathfrak{t}[u], \quad u \in \mathcal{D}(\mathfrak{t}).$$

The notions we built in the previous sections still apply here.

Definition 1.20. A sesquilinear form $\mathfrak{t}'$ is said to be *relatively bounded with respect to a given sesquilinear form* $\mathfrak{t}$, or simply $\mathfrak{t}$-*bounded*, if $\mathcal{D}(\mathfrak{t}') \supset \mathcal{D}(\mathfrak{t})$, and

$$|\mathfrak{t}'[u]| \leq a\|u\|^2 + b\, \mathfrak{t}[u], \quad u \in \mathcal{D}(\mathfrak{t}),$$

where $a, b \geq 0$. The $\mathfrak{t}$-*bound* of $\mathfrak{t}'$ is then the infimum of b that satisfies the bound.

We retain similar notions of closedness and closeability as with operators. However, sesquilinear forms make the sequential definition far easier to work with.

Definition 1.21. We say that a densely defined sesquilinear form $\mathfrak{t}$ on $\mathcal{H}$ is closed, if for any Cauchy sequence $\{u_n\}_{n\in\mathbb{N}} \in \mathcal{D}(\mathfrak{t})$:

$$u_n \to u, \quad \mathfrak{t}[u_n - u_m] \to 0, \quad \text{implies} \quad u \in \mathcal{D}(\mathfrak{t}), \quad \mathfrak{t}[u_n - u] \to 0.$$

We then call a sesquilinear form $\mathfrak{t}$ closeable if

$$u_n \to 0, \quad \mathfrak{t}[u_n - u_m] \to 0, \quad \text{implies} \quad \mathfrak{t}[u_n] \to 0.$$

Let $\{u_n\}_{n\in\mathbb{N}}, \{v_n\}_{n\in\mathbb{N}} \in \mathcal{H}$ be Cauchy sequences such that for some $u, v \in \mathcal{H}$, $u_n \to u, v_n \to v$, and $\mathfrak{t}[u_n - u_m], \mathfrak{t}[v_n - v_m]$ both converge in norm to 0. Then, we define the closure $\bar{\mathfrak{t}}$ as

$$\bar{\mathfrak{t}}(u,v) = \lim_{n\to\infty} \mathfrak{t}(u_n, v_n), \tag{1.22}$$

where $\mathcal{D}(\bar{\mathfrak{t}})$ contains all such $u, v \in \mathcal{H}$. $\mathfrak{t}$ exists independant of the chosen approximating sequences.

We can begin to connect sesquilinear forms to unbounded operators via the form analogue for the Riesz representation theorem.

Theorem 1.23 (Representation Theorem)**.** *Let $\mathfrak{a}$ be a symmetric, closed, densely defined, coercive sesquilinear form on $\mathcal{H}$, with domain $\mathcal{D}(\mathfrak{a})$. Then, for $u \in \mathcal{D}(\mathfrak{a})$, there exists $w \in H$ such that*

$$\mathfrak{a}(u,v) := \langle w, v\rangle$$

for every v in a dense subset of $\mathcal{D}(\mathfrak{a})$. Defining $Au = w$, we obtain a self-adjoint operator $A : \mathcal{D}(A) \subset \mathcal{H} \mapsto \mathcal{H}$ such that $\mathcal{D}(A) \subseteq \mathcal{D}(\mathfrak{a})$, where the closure of $\mathcal{D}(A)$ is $\mathcal{D}(\mathfrak{a})$.

With this powerful tool, we can begin to extend properties derived from the sesquilinear form to the corresponding operator such as relative bounds and closedness.

Corollary 1.24. *Let $\mathfrak{t}$ be a coercive symmetric sesquilinear form and T the associated, symmetric operator such that $\mathcal{D}(\mathfrak{t}) = \mathcal{D}(T)$. Then, $\mathfrak{t}$ is closeable.*

Proof. Let T be a symmetric operator and let

$$\mathfrak{t}(w, v) = \langle Tw, v\rangle,$$

where $\mathcal{D}(\mathfrak{t}) = \mathcal{D}(T)$. Because we assume $\mathfrak{t}$ to be coercive, we use Theorem 1.23 to state that T is uniquely associated to $\mathfrak{t}$. Let $\{u_n\} \in \mathcal{D}(\mathfrak{t})$ and assume $u_n \to 0$ and $\mathfrak{t}[u_n - u_m] \to 0$. By the definition of closeability, we want to show this implies

$$\lim_{n\to\infty} \mathfrak{t}[u_n] = 0.$$

We use the graph norm of $\mathfrak{t}$ as follows:

$$\|u\|_{\mathfrak{t}} = \|u\|_{\mathcal{H}} + \|Tu\|_{\mathcal{H}}.$$

By assumption, u_n converges in this norm to 0. Additionally, by Lemma 1.8 it follows that Tu_n also converges in norm to 0. Therefore, t is closeable.

Now, from (1.22) we wish to find some $\bar{\mathfrak{t}}$ such that for $\{w_n\}, \{v_n\}$ converging in norm to w, v respectively, but $w, v \notin \mathcal{D}(T)$, we have

$$\bar{\mathfrak{t}}(w, v) = \lim_{n\to\infty} \mathfrak{t}(w_n, v_n) = \lim_{n\to\infty} \langle Tw_n, v_n\rangle.$$

It follows that $(w, Tw), (v, Tv)$ are elements of the closure of $\mathcal{G}(T)$. Therefore, since symmetric forms are always closeable by Lemma 1.8, $\overline{T}$, the closure of T, is well defined. Therefore, $\mathfrak{t}$ is closeable as required. □

Henceforth, we refer to such a $\overline{T}$ associated with $\bar{\mathfrak{t}}$ the *Friedrichs extension* of T. We will see with the hydrogen Schrödinger operator that there are operators whose closures are only well defined when associated with a sesquilinear form. However, $\mathcal{D}(\overline{T})$ may not continue coinciding with $\mathcal{D}(\mathfrak{t})$, such as in the case of the Laplacian operator we will consider later.

1.4. **Spectral Theory.** We now recall the spectral theory for unbounded operators, following §32 [7].

Let $T : \mathcal{D}(T) \subset \mathcal{H} \mapsto \mathcal{H}$ be a densely defined operator. A complex number $\lambda \in \mathbb{C}$ is said to be a spectral point of T, if there is no bounded inverse $(T - \lambda I)^{-1} : \mathcal{H} \mapsto \mathcal{D}(T) \subset \mathcal{H}$ defined on the whole of $\mathcal{H}$. The spectral set of T is denoted as $\sigma(T)$. The resolvent set $\rho(T)$ is the set of all $\lambda \in \mathbb{C}$ such that $(T - \lambda I)^{-1}$ is well defined. Namely, $\rho(T) = \mathbb{C} \setminus \sigma(T)$.

The resolvent of T is an operator-valued function defined for the variable $z \in \rho(T) \subset \mathbb{C}$:

$$\mathcal{R}(T, z) := (T - zI)^{-1}. \tag{1.25}$$

Given $\lambda \in \sigma(T)$, we distinguish the following cases:

(1) The point spectrum $\sigma_{\mathrm{p}}(T)$ is the set of eigenvalues $\lambda \in \mathbb{C}$ of T with finite multiplicity.
(2) The essential spectrum $\sigma_{\mathrm{ess}}(T)$ is the set of points $\lambda \in \mathbb{C}$ such that either the null space of $T - \lambda I$ is infinite dimensional, or the range of $T - \lambda I$ is not a closed subspace of $\mathcal{H}$.

There are several results from finite-dimensional linear algebra that we want to generalize to infinite-dimensional spaces.

Theorem 1.26. *Let $\mathfrak{t}$ be a symmetric, closed, densely defined, coercive sesquilinear form with associated self-adjoint operator $T : \mathcal{D}(T) \subset \mathcal{H} \to \mathcal{H}$. Further, assume $\sigma(T)$ is bounded from below and for all $\lambda_1 \in \sigma_{\mathrm{p}}(T), \lambda_2 \in \sigma_{\mathrm{ess}}(T)$, $\lambda_1 \leq \lambda_2$. Then,*

$$\inf_{u \in \mathcal{D}(T), \|u\|=1} \mathfrak{t}[u] = \inf \sigma_{\mathrm{p}}(T).$$

One can interpret this theorem as a infinite-dimensional generalization of the min-max theorem from finite-dimensional linear algebra. This comes as a consequence of Theorem 6.1 in [4]. This gives us an important corollary for defining a generalized inverse operator.

Corollary 1.27. *Let $T : \mathcal{D}(T) \subset \mathcal{H} \to \mathcal{H}$ be a self-adjoint operator associated to a positive sesquilinear form $\mathfrak{t}$ where $\mathcal{R}(T)$ is the range of T. Then there exists an operator $T^{-1} : \mathcal{R}(T) \to \mathcal{D}(T)$ satisfying*

$$T(T^{-1}) = I : \mathcal{D}(T) \to \mathcal{D}(T). \tag{1.28}$$

Proof. For $\mathfrak{t}$ to be positive, there must exist some $\alpha > 0$ such that

$$\inf_{u \in \mathcal{D}(T), \|u\|=1} \mathfrak{t}[u] \geq \alpha > 0.$$

By Theorem 1.26, this means

$$\inf \sigma(T) \geq \alpha > 0.$$

This necessarily implies that $\ker(T) = \{0\}$. Because T is injective, there exists some injective operator $T^{-1} : \mathcal{D}(T^{-1}) \subset \mathcal{H} \mapsto \mathcal{H}$, where $\mathcal{D}(T^{-1})$ is equal to the range of T, such that

$$T(T^{-1}) = I$$

which maps $u \mapsto u$ as required. $\square$

We now cite the 2nd Kato-Rellich theorem from [9], whose content justifies the terminology *relative compactness*: the essential spectrum is stable under compact perturbations, while the point spectrum may vary.

Theorem 1.29 (Kato-Rellich Theorem II)**.** *Let T be self-adjoint and A be T-compact. Then $\sigma_{\mathrm{ess}}(T) = \sigma_{\mathrm{ess}}(T + A)$.*

We present one last, important theorem on the spectra of self-adjoint operators.

Theorem 1.30. *Self-adjoint operators have closed, real spectra.*

Although this is a mathematical paper, we admit that the operators we will be working with have physical meanings, and so should their eigenvalues. We thus want operators to be self-adjoint, so that all possible eigenvalues are real, therefore of concrete physical meanings.

2. Perturbation Theory

In this section, we present the basic aspects of analytic perturbation theory in Hilbert spaces. We will be considering an *operator-valued function* $T(\kappa)$, where κ varies in some domain $\Omega \subset \mathbb{C}$. It is called the *perturbation parameter*.

For bounded operators, there is already a holomorphic functional calculus closely paralleling single-variable complex analysis. However, when dealing with unbounded operators, the operator norms are typically not defined. Therefore, we will need broader notions of being holomorphic. Here, we discus holomorphic families that may not be holomorphic in the operator norm, but are still holomorphic in the strong or weak topology.

2.1. **Homomorphic Families of Type (A).** This is the first of two useful holomorphic families we will consider in the paper. These definitions and theorems are directly cited from sections VII §§1.2 and 2.1-2 of [6]. The operator-valued function T is given by

$$T : \big(\Omega \subset \mathbb{C}, \mathcal{D}(T) \subset \mathcal{H}\big) \to \mathcal{H},$$

where Ω is a domain in the complex plane where the "perturbation parameter" varies. But for notational simplicity, we shall consider instead $\mathcal{D}(T(\kappa))$, the domain of the κ-dependent family of operators. The following definition comes from Chapter VII.2 in [6].

Definition 2.1. A family $T(\kappa)$ of densely defined operators on $\mathcal{H}$ is said to be holomorphic of type (A) if:

- $\mathcal{D}(T(\kappa)) = \mathcal{D}$ is independent of κ.
- $T(\kappa)u$ is holomorphic for $\kappa \in \Omega$ for every $u \in \mathcal{D}$. This is known as *point-wise analyticity.*

Recalling the definition of vector-valued holomorphy, $T(\kappa)$ is holomorphic on Ω if for every fixed $u \in \mathcal{D}$,

$$\lim_{z\to\kappa} \frac{T(z)u - T(\kappa)u}{z-\kappa}$$

exists in $\mathcal{H}$. Then, the map $u \mapsto \lim_{z\to\kappa} \frac{T(z)u-T(\kappa)u}{z-\kappa}$ defines a linear operator $T'(\kappa) : \mathcal{D} \mapsto \mathcal{H}$ we call the derivative of $T(\kappa)$. Convergence is then taken *in the strong topology* for fixed $u \in \mathcal{D}$. This definition of holomorphy is convenient because it allows for a point-wise Taylor expansion of $T(\kappa)u$. That is, for each $\kappa_0 \in \Omega$, we can write for κ in some small disk centered at κ_0,

$$\begin{aligned} T(\kappa)u &= \sum_{n=0}^{\infty} (\kappa-\kappa_0)^n T^{(n)}u \\ &= T^{(0)}u + (\kappa-\kappa_0)T^{(1)}u + (\kappa-\kappa_0)^2 T^{(2)}u + \cdots \quad u \in \mathcal{D}. \end{aligned} \tag{2.2}$$

In fact, we can formulate a criterion of (A)-holomorphicity, which tells us that the power series (2.2) has a convergence radius independent of $u \in \mathcal{D}$.

Theorem 2.3. *Let $T^{(0)}$ be a closable operator with $\mathcal{D}(T^{(0)}) = \mathcal{D}$. Let $T^{(n)}$, $n = 1, 2, \ldots$, be densely defined operators with domains containing $\mathcal{D}$, and suppose there are constants $a, b, c \geq 0$ such that*

$$\left\|T^{(n)}u\right\| \leq c^{n-1}\left(a\|u\| + b\left\|T^{(0)}u\right\|\right), \quad u \in D,\ n = 1, 2, \ldots \tag{2.4}$$

where the bound is uniform in n but exponential in c. Then, (2.2) defines an operator $T(\kappa)$ with domain $\mathcal{D}$ for $|\kappa| < 1/c$. If $|\kappa| < (b+c)^{-1}$, then $T(\kappa)$ is closable and the closures $\overline{T}(\kappa)$ for such κ form a holomorphic family of type (A).

The series (2.4) is greatly simplified in case $T^{(2)} = T^{(3)} = \cdots = 0$, namely, when $T(\kappa)$ is formally linear in κ. In this case we can choose $c = 0$ and require only

$$\left\|T^{(1)}u\right\| \leq a\|u\| + b\left\|T^{(0)}u\right\|, \quad u \in \mathcal{D}. \tag{2.5}$$

Therefore, our definition of relative boundedness from (1.14) extends to defining holomorphic families as well. This is not a coincidence, as one should consider this a generalization of Cauchy's estimate for Taylor expansions of holomorphic functions.

2.2. **Holomorphic Families of Type (B).** These definitions and theorems are directly cited from VII §§4.1-2 and 4.5 in [6]. Like operators, we can define holomorphic families of sesquilinear forms $\{\mathfrak{t}(\kappa)\}$ by taking assumptions similar to those of A-holomorphicity.

Definition 2.6. A family $T(\kappa)$ of densely defined operators on $\mathcal{H}$ is said to be *holomorphic of type (B)* if:

- $T(\kappa)$ is the operator associated with a family of densely defined sesquilinear forms $\mathfrak{t}(\kappa)$, whose domain in $\mathcal{H}$, $\mathcal{D}$, is independent of κ.
- For each fixed $u, v \in \mathcal{D}(\mathfrak{t})$, $\mathfrak{t}(\kappa)(u, v)$ is holomorphic.

Like with the A-holomorphic operator, for each fixed $u, v \in \mathcal{D}(\mathfrak{t})$ we may expand $\mathfrak{t}$ into a convergent power series in κ

$$\mathfrak{t}(\kappa)(u, v) = \mathfrak{t}(u, v) + \kappa\mathfrak{t}^{(1)}(u, v) + \kappa^2\mathfrak{t}^{(2)}(u, v) + \cdots .$$

It is important to mention that this is still a notion of holomorphicity in the weak sense.

Generally, there is no special relationship between holomorphic families of type (A) and (B). There is for a *self-adjoint* family of type (A).

Theorem 2.7. *If a holomorphic family $T(\kappa)$ of type (A) is self-adjoint for κ in a neighborhood of the real axis and is bounded from below for some real κ, then it is a holomorphic family of type (B). Additionally, the $T^{(n)}$'s in the power series (2.2) satisfy*

$$\left|\langle T^{(n)}u, u\rangle\right| \leq c^{n-1}\left(a\|u\|^2 + b\,\mathrm{Re}\langle T^{(0)}u, u\rangle\right), \quad u \in \mathcal{D}, \tag{2.8}$$

with constants $a \geq 0$ and $0 \leq b < 1$.

We can similarly set $c = 0$ if $T^{(n)} = 0$ for $n > 1$ as in (2.5). In this case, we obtain

$$\left|(T^{(1)}u, u)\right| \leq a\|u\|^2 + b\,\mathrm{Re}\langle T^{(0)}u, u\rangle. \tag{2.9}$$

2.3. **Eigenprojections.** As we previously explained, the power series of $T(\kappa)$ converges (in a weaker sense) within some radius of convergence ρ. Without loss of generality, suppose that we are considering κ varying within a neighbourhood of $0 \in \mathbb{C}$. We are interested in how the isolated eigenvalues of $T(\kappa)$ change with respect to κ. Within the scope of this paper, we will only deal with simple eigenvalues. These definitions and theorems are directly cited from sections VII §4.6 of [6].

This is where the resolvent operator comes into play. We take (1.25) and modify it only to include the dependence on κ, giving us

$$\mathcal{R}(T(\kappa), z) = \big(T(\kappa) - zI\big)^{-1}.$$

As long as we look at a punctured domain and the resolvent set $\rho(T(\kappa))$, the operator-valued function $\mathcal{R}(T(\kappa), z)$ is jointly holomorphic in both variables κ, z, in the usual, strong sense at least within some radius of convergence ρ_0. The singularities of $\mathcal{R}(T(\kappa), z)$ correspond exactly to the spectrum of $T(\kappa)$.

Theorem 2.10. *Let $T(\kappa)$ be a holomorphic family of type (A) or (B). Let $\mathcal{R}(T(\kappa), z)$ be the corresponding resolvent operator. Assume that $T(0)$ has a simple eigenvalue λ. Let Γ be a contour that separates λ from the rest of $\sigma(T(0))$ where $\Gamma \cap \sigma(T(0)) = \emptyset$. Then the bounded linear operator*

$$P(\kappa) := \frac{1}{2\pi i} \oint_{\Gamma} \mathcal{R}(T(\kappa), z) dz \tag{2.11}$$

is holomorphic in the operator sense in κ, and is indeed a projection operator onto the eigenspace of $\lambda(\kappa)$. Specifically, $P(\kappa)$ has a series expansion that converges for $|\kappa| < \rho_0$, the same radius as $\mathcal{R}$.

Proof. We take $T(\kappa), \mathcal{R}(T(\kappa), z), \lambda(\kappa), \Gamma$ as stated in Theorem 2.10. By the Cauchy Residue theorem

$$P(\kappa) = \frac{1}{2\pi i} \oint_{\Gamma} \mathcal{R}(T(\kappa), z) dz = \operatorname{Res}(\mathcal{R}(T(\kappa), z), \lambda(\kappa)).$$

At the singularity, $\mathcal{R}(T(\kappa), z)$ now becomes a meromorphic function which we separate into the principal part and the holomorphic part

$$\sum_{i=1}^{m} \frac{A_i}{(z-\lambda)^i} + A_0. \tag{2.12}$$

m is the algebraic multiplicity of the eigenvalue. This decomposition is only well defined if we assume that the singularity maintains a fixed multiplicity. To ensure this is the case, assume $\lambda(\kappa)$ is simple. The residue corresponds to A_1 in (2.12), which can be obtained via

$$\lim_{z \to \lambda} (z-\lambda)(T(\kappa) - zI)^{-1}.$$

It exists via l'Hôpital's rule.

We now show this is a projective operator via $P^2 = P$. By Hilbert's identity and the Cauchy integral formula,

$$P^2 = \left(\frac{1}{2\pi i}\right)^2 \oint_{\Gamma} \oint_{\Gamma} \frac{\mathcal{R}(T(\kappa), z) - \mathcal{R}(T(\kappa), w)}{z-w} dz dw = \frac{1}{2\pi i} \oint_{\Gamma} \mathcal{R}(T(\kappa), w) dw. \tag{2.13}$$

Therefore, $P(\kappa)$ is indeed a projection operator. Given this is a projection operator corresponding to an eigenvalue, it follows that $P(\kappa)$ projects onto the eigenspace of $\lambda(\kappa)$.

We now must show $P(\kappa)$ is holomorphic. Take a compact domain $U \subset \mathbb{C}$ and fix $k_0 \in U$. For a compact domain $U \times \Gamma$ where joint holomorphicity applies, the resolvent is continuous, which implies the uniform bound

$$\|\mathcal{R}(T(\kappa), z)\| \leq M. \tag{2.14}$$

Assume $|\Gamma| = L$. Then we get

$$|P(\kappa)| = \left| \frac{1}{2\pi i} \oint_{\Gamma} \mathcal{R}(T(\kappa), z) \right| \leq \frac{ML}{2\pi}.$$

By the holomorphicity of $\mathcal{R}(T(\kappa), z)$ and the uniform bound, $P(\kappa)$ is continuous.

By assumption, (2.5) holds, which means there exists some C such that the following uniform bound holds

$$\|\partial_\kappa T(\kappa)\| \leq C.$$

This means the derivative of the resolvent is also uniformly bounded

$$\|\partial_\kappa (T(\kappa) - zI)^{-1}\| = \left\| -(T(\kappa) - zI)^{-1}(\partial_\kappa T(\kappa))(T(\kappa) - zI)^{-1}\right\| \leq CM^2.$$

where in the last step we used (2.14). Because $\partial_\kappa T(\kappa)$ is uniformly bounded, in $\partial_\kappa P(\kappa)$ we can interchange the integral and derivative. Taking the bound once more,

$$|\partial_\kappa P(\kappa)| = \left|\frac{1}{2\pi i}\oint_\Gamma \partial_\kappa \mathcal{R}(T(\kappa), z)\right| \leq \frac{LCM^2}{2\pi}.$$

Therefore, $P(\kappa)$ is holomorphic, so we can also expand it into a Taylor series. To determine the radius of convergence we note that in II.3 of [6], Kato derives

$$\mathcal{R}(T(\kappa), z) = \mathcal{R}(T(0), z)\left[I + \left(\sum_{n=0}^{\infty} \kappa^n T^{(n)}\right)\mathcal{R}(T(0), z)\right]^{-1}.$$

The power series in the above will then converge if

$$\left\|\left(\sum_{n=0}^{\infty} \kappa^n T^{(n)}\right)\mathcal{R}(T(0), z)\right\| < 1.$$

By the triangle inequality,

$$\left\|\left(\sum_{n=0}^{\infty} \kappa^n T^{(n)}\right)\mathcal{R}(T(0), z)\right\| \leq \sum_{n=1}^{\infty} |\kappa|^n \left\|T^(n)\mathcal{R}(T(0), z)\right\|.$$

To ensure convergence, we then require that $|\kappa| < 1$. The contour Γ is compact, guaranteeing a minimum $z \in \Gamma$, which we call ρ_0. If we assume that $|z| < 1$, then

$$|\kappa| < \rho_0 = \min_{z\in\Gamma} |z|$$

gives a uniform lower bound for the convergence of $\mathcal{R}(T(\kappa), z)$ by the Weiertrass M-test. Because of its dependence on $\mathcal{R}(T(\kappa), z)$, $P(\kappa)$ has the same radius of convergence ρ_0 as required. □

Therefore, to determine the radius of analyticity ρ_0 for $\mathcal{R}(T(\kappa), z)$ we can solve ρ_0 for $P(\kappa)$. Finally, for type (B) operators, ρ_0 can be written as

$$\begin{aligned}\rho_0 &= \inf_{z\in\Gamma} \left(\varepsilon\|(a + bT(\kappa))\mathcal{R}(T(\kappa), z)\| + c\right)^{-1} \\ &= \inf_{z\in\Gamma} \inf_{\lambda\in\sigma(T(\kappa))} \left(\varepsilon\left|\frac{a + b\lambda}{\lambda - z}\right| + c\right)^{-1}.\end{aligned} \tag{2.15}$$

There exists a similar result for type (A) operators that are not also type (B), but this is a far cleaner (and easier) way to derive the radius of convergence. It also follows that since the essential spectrum of T corresponds to the essential singularities of $\mathcal{R}(T(\kappa), z)$, the Casorati-Weierstrass theorem thwarts any attempt at acquiring a well-defined projection operator.

Kato also shows that the eigenvalues $\lambda(\kappa)$ themselves may be holomorphic. Given the definition of $P(\kappa)$ we may define $\lambda(\kappa)$ as

$$\lambda(\kappa) := \frac{1}{2\pi i}\oint_\Gamma z\mathcal{R}(T(\kappa), z)dz.$$

To deal with eigenvalue crossings and branching, one generally defines a fractional Puiseux series. If one only considers a simple eigenvalue, then $\lambda(\kappa)$ is actually analytic and admits a perturbation series

$$\lambda(\kappa) = \lambda^0 + \sum_{n=1}^{\infty} \kappa^n \lambda^{(n)}.$$

For both series, the radius of convergence is still ρ_0. Now we admit another fantastic consequence of self-adjoint operators. According to lemma 1 in [8], if a power series of κ converges for $|\kappa| < \rho_0$ and is similarly convergent for real $|\beta| < \rho_0$, then it is real-holomorphic on the real line. We then recall Theorem 1.30 and see that for simple $\lambda(\kappa)$, we may analytically continue it on the entire real line. When we consider the 2-electron problem later, we are fundamentally interested in the spectrum and convergence of the eigenvalues, and it is merely that the resolvent and projections (2.15) offer a convenient way to analyze their convergence and behavior that we use these methods.

3. The Hydrogen Atom

For the remainder of the paper, we will work with the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$. The most important operator in this space that we will analyze is the Schrödinger operator for a *dimensionless* single electron atom. Namely,

$$S = -\Delta - \frac{1}{|x|}, \quad x \in \mathbb{R}^3. \tag{3.1}$$

where Δ denotes the Laplacian operator. More specifically, we want to understand its spectrum. We note that *in quantum mechanics*, this operator normally involves several physical parameters

$$H = -\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{4\pi\varepsilon_0 |x|}. \tag{3.2}$$

We shall refer H as the Hamiltonian operator for the (quantum) hydrogen atom system. The parameters $\hbar, \mu, e, \varepsilon_0$ are of clear physical meaning:

- $\hbar$: reduced Planck constant.
- μ: reduced mass of electron.
- e: charge of electron.
- ε_0: vacuum permittivity.

The Hamiltonian operator is one of the most important operators in quantum mechanics, since it describes the total energy of a given system. $-\frac{\hbar^2}{2\mu}\Delta$ denotes the kinetic energy or momentum of the particle, and in the case of the hydrogen atom, $-\frac{e^2}{4\pi\varepsilon_0|x|}$ denotes the potential energy, or the energy of the system. The spectrum of H then corresponds to the possible energy levels the electron can take within the system, which is fundamentally the most important concept in Physics that we are concerned with.

We define a unitary dilation operator $\mathcal{L} : \mathcal{H} \to \mathcal{H}$, with the scaling factor to be determined later, such that $\mathcal{L}^{-1} H \mathcal{L}$ is a multiple of S. Therefore, to understand the spectrum of H, it suffices to understand the spectrum of S. For the moment, it is not yet known if S is self-adjoint. This is an immense issue since if the spectrum is not real, the eigenvalues (hence the energy levels) are complex, which make little physical sense. As such, we want to show that S (hence H) is a self-adjoint operator.

3.1. **Step 1: The Sesquilinear Form of the Laplacian.** Here, we show the true power of a sesquilinear form, especially in the context of exploring the properties of an operator like the Laplacian.

Theorem 3.3. *There exists a unique Friedrich's extension of $-\Delta$ that is self-adjoint.*

Proof. Let us define Δ first on the dense domain $C_0^\infty(\mathbb{R}^3) \subset H_0^1$, where the latter is itself a dense subspace of $L^2(\mathbb{R}^3)$. For $u, v \in C_0^\infty(\mathbb{R}^3)$, we use Green's identity

$$\langle u, -\Delta v\rangle_{L^2} = \int_{\mathbb{R}^3} u \cdot (-\Delta v) = \int_{\mathbb{R}^3} \nabla v \cdot \nabla u = \int_{\mathbb{R}^3} -\Delta u \cdot v = \langle -\Delta u, v\rangle_{L^2}.$$

This is possible due to compact support. This tells us two major things:

(1) $-\Delta$ is symmetric. However, as long as we put restrictions on the domain of $-\Delta$, the dual domain is $H^2(\mathbb{R}^3)$, the 2nd Sobolev space, which is indeed a superset of $C_0^\infty(\mathbb{R}^3)$. Elements in $H^2(\mathbb{R}^3)$ are not restricted to compact support nor need even be differentiable in the classical sense, but "weakly" differentiable. Therefore, $-\Delta$ is symmetric but not self-adjoint.

(2) We can associate $\langle -\Delta u, v\rangle$ with the sesquilinear form:

$$\mathfrak{a}(v, u) := \langle \nabla v, \nabla u\rangle_{L^2}.$$

The form $\mathfrak{a}$ is not closed, but due to Theorem 1.24, it is still closeable (recall $\mathfrak{a}[u]$ is non-negative).

Our strategy is then to extend $-\Delta$ to a self-adjoint operator by first extending $\mathfrak{a}$ to the Sobolev space $H_0^1(\mathbb{R}^3)$, the closure of $C_0^\infty(\mathbb{R}^3)$ under the norm

$$\|u\|_{H^1}^2 := \|\nabla u\|_{L^2}^2 + \|u\|_{L^2}^2. \tag{3.4}$$

The corresponding Friedrich's extension $-\tilde{\Delta}$ will be called the "weak Laplacian." To justify this naming, we examine the graph norm associated to $\tilde{\Delta}$:

$$\|u\|_{-\tilde{\Delta}}^2 = \|u\|_{L^2}^2 + \|\tilde{\Delta} u\|_{L^2}^2.$$

This coincides with the H^2 norm, so $\mathcal{D}(-\tilde{\Delta})$ is $H^2(\mathbb{R}^3)$. Technically, it is actually $H^2 \cap H_0^1$, but if we are considering functions defined over all of $\mathbb{R}^3$, then H^2 is a strict subset of H_0^1. It is still dense within H_0^1 since

$$C_0^\infty(\mathbb{R}^3) \subset H^2(\mathbb{R}^3) \subset H_0^1(\mathbb{R}^3). \tag{3.5}$$

Similarly, the dual spaces of Sobolev spaces have the inverse inclusion $H^{-2} \cap H^{-1} = H^{-1}$.

Accordingly, we define the closed extension

$$\langle -\tilde{\Delta} u, v\rangle_{H^{-1}, H^2} = \tilde{\mathfrak{a}}(v, u) = \langle v, u\rangle_{H_0^1}. \tag{3.6}$$

The form $\tilde{\mathfrak{a}}$ is defined on all of H_0^1, therefore densely defined on L^2. By definition, $\langle u, u\rangle_{H_0^1}$ is coercive. By the Representation Theorem 1.23, $-\tilde{\Delta}$ is the self-adjoint operator satisfying (3.6). There then exists a uniquely defined $w = -\tilde{\Delta} u$ where $w \in L^2$ as required. For notational simplicity, we shall henceforth only use $-\Delta$ with the caveat that this always refers to the weak Laplacian. $\square$

3.2. **Step 2: Relative Compactness of the Coulomb Potential.** We now return to the Schrödinger operator:

$$S = -\Delta + q(x)$$

where for now, $q(x)$ is some arbitrary potential function. The following two sections will follow V §§5.1-3 in [6]. We have extended $-\Delta$ into a self-adjoint operator, but we need to check that the Coulomb perturbation has a satisfactory relative bound with respect to the Laplacian. To this end, Kato derives Lemma 5.8 and Theorem 5.7.

Theorem 3.7. *Consider $S = -\Delta + q(x)$, where the potential*

$$q(x) = q_0(x) + q_1(x) \tag{3.8}$$

is such that $q_0(x) \in L^\infty$, and $q_0(x) \to 0$ when $|x| \to \infty$, while $q_1(x) \in L^2$. Then S is bounded from below and $q(x)$ is $-\Delta$-compact with $-\Delta$-bound 0.

Now, we prove the following important lemma to show that the Coulomb potential satisfies the given criteria of Theorem 3.7.

Lemma 3.9. *Let $q(x) = \frac{1}{|x|^\beta}$ where $\beta > 0$ and $x \in \mathbb{R}^3$. Then, $q(x)$ satisfies (3.8) for any $\beta < 1.5$.*

Proof. We want to split q into a q_0 and q_1. To accomplish this, we consider a smooth, compactly supported function $b(x)$ that equals 1 when $|x| \leq 1$ and vanishes when $|x| \geq 2$. We then split

$$q(x) = q(x)(1 - b(x)) + q(x)b(x) =: q_0(x) + q_1(x). \tag{3.10}$$

$q_0(x)$ is smooth and tends to zero when $|x| \to \infty$. As for the function $q_1(x)$, we observe that the singularity at $x = 0$ does not destroy its L^2 integrability: the L^2 norm

$$\int_{\mathbb{R}^n} |q(x)b(x)|^2 \mathrm{d}x$$

is computed under the polar coordinates as

$$C_n \int_{\mathbb{R}^+} |r|^{-2\beta} b(r)^2 r^2 \mathrm{d}r \leq C_n \int_0^2 |r|^{(2-2\beta)} \mathrm{d}r \tag{3.11}$$

where C_n is a dimensional constant. Since $\beta < 1.5$, this last integral is convergent. This shows that $q_1 \in L^2$. □

Therefore, the Coulomb potential has Δ-bound 0. By Theorem 1.18, the Schrödinger operator is self-adjoint. This decomposition works for the single-electron Coulomb potential but fails in the two-electron case, where the stronger singularity leads to divergence. We will return to this issue later.

3.3. **Step 3: The Spectrum.** In this stage, we can now analyze the spectrum of the Schrödinger operator:

Theorem 3.12. *Let S be the dimensionless Schrödinger operator defined in (3.1). The essential and point spectrum of S are respectively*

$$\sigma_{\mathrm{ess}}(S) = [0, +\infty), \quad \sigma_{\mathrm{p}}(S) = \left\{ -\frac{1}{(n+1)^2} : n \in \mathbb{N} \cup \{0\} \right\}. \tag{3.13}$$

Proof. First, we admit that by the Fourier-Plancherel theorem, there is a linear isometric map $\mathcal{F} : \mathcal{H} \to \mathcal{H}$, defined by

$$\mathcal{F}u(k) = \hat{u}(k) := \int_{\mathbb{R}^3} u(x)e^{ix\cdot k}dx, \quad u \in H^2(\mathbb{R}^3).$$

For $u \in H^2(\mathbb{R}^3)$, a direct computation via Green's formula gives

$$\mathcal{F} : -\Delta u \to |k|^2\hat{u}(k), \quad u \in H^2(\mathbb{R}^3). \tag{3.14}$$

This shows that $-\Delta$ indeed is conjugated to a multiplicative operator via the Fourier transform. By the properties of multiplicative operators, the spectrum of $-\Delta$ is the essential range of $|k|^2$, which in this case is $\mathbb{R}^+$. Therefore,

$$\sigma_{\text{ess}}(T) = [0, \infty).$$

A would-be square-integrable function $f(x)$ of $-\Delta$ must satisfy $|k|^2\hat{f}(k) = \lambda\hat{f}(k)$. This shows that the Fourier support of $\hat{f} \in L^2(\mathbb{R}^3)$ must be contained in the sphere $|k| = \sqrt{\lambda}$, which is of Lebesgue measure zero, leading to a contradiction. Therefore, $-\Delta$ has no point spectrum.

Now, we consider the full operator S. As indicated by Theorem 3.7, because the Coulomb potential vanishes at infinity, it is Δ-compact. As such, by 3.7, S is self-adjoint. By Theorem 1.29, $\sigma_{\text{ess}}(S) = \sigma_{\text{ess}}(-\Delta)$.

As for the point spectrum, we in fact have the following famous *Bohr Formula*: the point spectrum of S (which we henceforth call the "energy levels") consists exactly of

$$E_n := -\frac{1}{(n+1)^2}, \quad n \in \mathbb{N} \cup \{0\}. \tag{3.15}$$

The eigenfunctions corresponding to E_n are given by

$$\Psi_{n\ell m}(r,\theta,\varphi) := \sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-\rho/2}\, \rho^\ell\, L^{2\ell+1}_{n-\ell-1}(\rho)\, Y^m_\ell(\theta,\varphi), \tag{3.16}$$

where

- $\rho = 2r/(na_0^*)$, with $a_0^* = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ being the reduced Bohr radius.
- $L^{2\ell+1}_{n-\ell-1}$ is the standard generalized Laguerre polynomial of degree $n-\ell-1$.
- Y^m_ℓ is the standard spherical harmonic function of degree ℓ and order m.
- The multiplicity of each energy level E_n is n^2.

The derivation is well known, and we encourage the reader to refer to [5] or their favorite quantum mechanics textbook. By convention, each $\Psi_{n\ell m}$ is called an "eigenstate." Ψ_{000} is then called the *ground state* with the corresponding energy level E_0 called the ground state energy.

□

Remark 3.17. Physically speaking, via the Fourier transform, we can infer that the continuous spectrum refers to particles that are in free motion. These are so-called "scattering" states. On the other hand, the addition of the Coulomb potential causes states to have a localized radial position in space, bounding them in a potential "well." Electrons are forced to exist in discrete bands around the nucleus, so we call these the "bound states." For the purpose of the one- and two-electron problems, we assume *a priori* that no outside influence is affecting the potential, such that we *only* care about the point spectrum.

3.4. **Step 4: Scaling of the Hamiltonian.** The attentive reader might realize that the given formulas for the energy and eigenstates in (3.16) and (3.15) are not as usually presented. Notably, they are scaled down! Let us finally show how to pass from the spectrum of S to the spectrum of H, the "physical" Schrödinger operator in (3.1).

Corollary 3.18. *Given $\alpha, \beta > 0$, let $\mathcal{L}_{\alpha,\beta}$ be the unitary dilation operator on $\mathcal{H}$ defined by*

$$(\mathcal{L}_{\alpha,\beta}u)(x) := \left(\frac{\beta}{\alpha}\right)^{3/2} u\left(\frac{\alpha}{\beta}x\right).$$

Then the rescaled operator

$$S_{\alpha,\beta} := -\alpha\Delta - \frac{\beta}{|x|} \tag{3.19}$$

satisfies $S_{\alpha,\beta} = (\beta^2/\alpha)\mathcal{L}_{\alpha,\beta}^{-1} S \mathcal{L}_{\alpha,\beta}$. Consequently, the spectrum of the left-hand-side of (3.19) reads

$$\sigma_{\mathrm{p}}(S_{\alpha,\beta}) = \left\{\frac{\beta^2}{\alpha}E_n : n \in \mathbb{N}_0\right\}, \quad \sigma_{\mathrm{ess}}(S_{\alpha,\beta}) = [0, +\infty) \tag{3.20}$$

Proof. We begin with the rescaled Schrödinger operator

$$S_{\alpha,\beta} = -\alpha\Delta - \frac{\beta}{|x|}.$$

We define $\mathcal{L}_{\alpha,\beta}$ by considering the rescaling $\tilde{x} = \frac{\alpha}{\beta}x$ which homogenizes the equation. As a result of this transformation, we have

$$-\alpha\Delta_x - \frac{\beta}{|x|} = \frac{\beta^2}{\alpha}\left[-\Delta_{\tilde{x}} - \frac{1}{|\tilde{x}|}\right]. \tag{3.21}$$

This is exactly the conjugation between $S_{\alpha,\beta}$ and S we are looking for, and solving for the spectrum gives us the desired spectrum result for $S_{\alpha,\beta}$.

Next, we investigate the eigenfunction scaling. We begin with any normalized eigenfunction $\Psi \in \mathcal{H}$ for $S_{\alpha,\beta}$:

$$\int_{\mathbb{R}^n} |\Psi(x)|^2 \, dx = 1. \tag{3.22}$$

Using the change-of-variable formula, we get

$$\int_{\mathbb{R}^n} |\Psi(\tilde{x})|^2 d\tilde{x} = \left(\frac{\beta}{\alpha}\right)^3. \tag{3.23}$$

From (3.22), it follows that

$$\Psi(x) = \left(\frac{\beta}{\alpha}\right)^{3/2} \Psi(\tilde{x}). \tag{3.24}$$

□

This justifies our usage of the dimensionless Schrödinger operator over the Hamiltonian operator. Considering (3.2), (3.15) and (3.16) are scaled down by exactly the Rydberg constant R and the Bohr radius a_0^* (to the -3/2 power) respectively. This scaling argument is an important step towards the 2-electron problem.

4. The Helium Atom

This section follows chapter VII §4.9 in [6]. We now visit the two-electron problem by defining the following Hamiltonian operator

$$H = -\frac{\hbar^2}{2m}\Delta_{x_1} - \frac{\hbar^2}{2m}\Delta_{x_2} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|x_1|} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|x_2|} + \frac{e^2}{4\pi\varepsilon_0|x_1-x_2|}, \quad x_1, x_2 \in \mathbb{R}^3,$$

which is defined on $\mathcal{H}\otimes\mathcal{H} \cong L^2(\mathbb{R}^6)$.The number $Z > 0$ corresponds to the number of protons in the nucleus, which in the helium atom case corresponds to $Z = 2$. In addition to the individual nuclear Coulomb interaction, we now also have the Coulomb interaction between the electron particles.

In Lemma 3.9, we were able to control the Coulomb singularity because it was an isolated point. However, the singularity set of $\frac{1}{|x_1-x_2|}$ is of co-dimension 3. The potential $\frac{1}{|x_1-x_2|}$ therefore falls out of the coverage of Theorem 3.7, which is a sufficient but not a necessary condition for self-adjointness. Therefore, we need to find some other way to show that S is self-adjoint.

Under the rescaling transformation discussed in Corollary 3.18, we find that H can be conjugated to the following dimensionless 2-electron Schrödinger operator:

$$S = -\Delta_{x_1} - \Delta_{x_2} - \frac{1}{|x_1|} - \frac{1}{|x_2|} + \frac{1}{Z}\frac{1}{|x_1-x_2|}. \tag{4.1}$$

We can then re-name the operators

$$\kappa := \frac{1}{Z}, \quad S^0 := -\Delta_1 - \frac{1}{|x_1|} - \Delta_2 - \frac{1}{|x_2|}, \quad S^1 := \frac{1}{|x_1-x_2|},$$

so that we end up with

$$S(\kappa) := S^0 + \kappa S^1.$$

Therefore, we may regard κS^1 as a perturbation of S^0. We shall justify shortly that it fits within our framework of the holomorphic families.

Theorem 4.2. *The operators $S(\kappa)$ form a self-adjoint family of (B) holomorphic operators. The ground state energy of S^0 is a holomorphic function of κ when $|\kappa| < \rho_0$ for some $\rho_0 > 0$. Specifically, ρ_0 is a lower bound for the radius of convergence of the ground state energy of $S(\kappa)$.*

Proof. We start by noting that $-\Delta_i - \frac{1}{|x_i|}$ acts on $\mathcal{H}_i$. Therefore, when taking the tensor product, each $-\Delta_i$ will act only on the vectors that act on that space. Therefore, the results of Lemma 3.9 are the same for each $\mathcal{H}_i$, so S^0 is still self-adjoint. This further implies that its eigenfunction inputs are non-interacting such that $\Psi(x_1, x_2) = \Psi(x_1)\Psi(x_2)$. This means that the energy is a sum of two copies of (3.15). The lowest energy levels are thus given by:

$$-\left(1 + \frac{1}{(n+1)^2}\right), \quad n \in \mathbb{N}\cup\{0\}. \tag{4.3}$$

To deal with $\frac{1}{|x_1-x_2|}$, This is a classical "two-body problem" in physics, so we perform the Jacobi coordinate

$$r := x_1 - x_2, \quad R := \frac{x_1+x_2}{2}, \tag{4.4}$$

giving us

$$\Delta_{x_1} + \Delta_{x_2} = 2\Delta_r + \frac{1}{2}\Delta_R.$$

Because $|x_1 - x_2| = |r|$ under this transformation, it follows that Δ_R acts trivially, leaving us with only $-\Delta_r - \frac{1}{|r|}$, which is an operator acting on $\{0\} \otimes \mathcal{H}_r$. Therefore, Lemma 3.9 still applies.

Corollary 1.15 implies that $\frac{1}{|r|}$ is also S^0-bounded with relative bound 0. Given (2.5), $S(\kappa)$ is then a holomorphic family of type (A). But if we recall Theorem 3.7 gives us a relative bound of 0, then Theorem 1.18 applies, making $S(\kappa)$ a self-adjoint (A)-holomorphic family. Therefore, we conclude that the ground state energy $E_0(\kappa)$ of $S(\kappa)$ is a holomorphic function of κ at least for $|\kappa| < \rho$.

We now want to find such a ρ by extending $S(\kappa)$ to a (B)-holomorphic family. Alongside Theorem 1.26, the correspondence between (A) and (B)-holomorphy in Theorem 2.7, guarantees the existence of sesquilinear forms associated with $S^0, S^1, S(\kappa)$, such that $S(\kappa)$ is (B)-holomorphic as well (on the real line). Furthermore, there exists $a \geq 0, 1 > b \geq 0$ such that (2.8) is fulfilled for S^1.

Since S^1 is non-negative, by definition it follows that for $u \in L^2$,

$$\langle S^0 u, u \rangle \leq \langle S(\kappa) u, u \rangle. \tag{4.5}$$

Therefore, the spectrum of S^0 represents a lower bound for the spectrum of $S(\kappa)$ by 1.26. Given (3.16), the only eigenstate Ψ_i for which the associated energy level E_i is simple is the ground state Ψ_0. We can then use Theorem 2.10 to calculate ρ_0 for $E_0^0(\kappa)$, with ρ_0 being a lower bound for ρ, from (2.15) as required. □

It is true that we know ρ_0 for $E_0^0(\kappa)$ to exist, but we did not explicitly show what the radius could be. Although it seems like we may have brushed it under the rug, it is actually because this is the most delicate step in the entire computation. It determines whether the ground state energy series converges for the most important, helium ($Z = 2$) case. The next chapter will cover the estimates for this ρ_0.

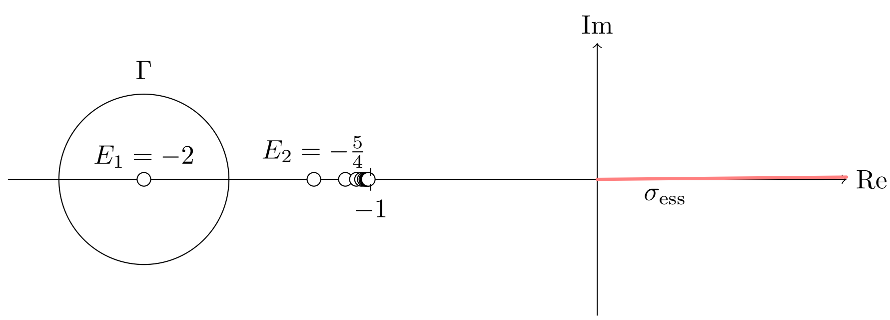

Figure 1. The spectrum of S^0, with σ_{p} following $-1 - \frac{1}{n^2}$, and $\sigma_{\text{ess}} = [0, \infty)$. The ground state energy $E_0 = -2$ is simple such that we may project onto it via Kato's methods.

5. Lower Bound for the Radius of Convergence

Although there is only one lower bound that has been found as of yet that works for the helium atom ($Z = 2$), we feel it is best if the reader is exposed to all the derivations so as to better understand the process of result refinements.

To use the tools developed for (B)-holomorphy, we define the comparison operator where we replace κ with an arbitrary $\beta > 0$

$$S_{\pm}(\beta) = S^0 \pm \beta S^1.$$

We prefer β because our results will only matter for real κ. Due to (4.5), we can produce only a coarse lower bound of E_0 for $S_+(\beta)$. It will be useful in securing a lower bound, but $S_-(\beta)$ will give us better relative bounds to calculate the radius of convergence (for now).

5.1. **Kato's original result.** We will first present Kato's first method. We consider a modified operator:

$$S_-(\alpha,\beta) = \left(-\alpha\Delta_1 - \frac{1}{|x_1|}\right) + \left(-\alpha\Delta_2 - \frac{1}{|x_2|}\right) + \left[-(1-\alpha)(\Delta_1+\Delta_2) - \frac{\beta}{|x_1 - x_2|}\right].$$

The rightmost term is currently not in the desired form, but we can use (4.4) to get $-2(1-\alpha)\Delta_r - 2|r|^{-1}$. Now, using Corollary 3.18, we find that the lowest eigenvalue of $S_-(\alpha,\beta)$ is

$$-\left(\frac{2}{\alpha} + \frac{\beta^2}{2(1-\alpha)}\right).$$

By Theorem 1.26, we get that the corresponding sesquilinear form of $S_-(\alpha,\beta)$ for $u \in L^2(\mathbb{R}^6)$ has the lower bound

$$\langle S_-(\alpha,\beta)u, u\rangle \geq -\left(\frac{2}{\alpha} + \frac{\beta^2}{2(1-\alpha)}\right)\langle u, u\rangle.$$

From this, we can establish a relative bound of the sesquilinear form of S^1

$$0 \leq \langle S^1 u, u\rangle \leq \frac{1}{\beta}\left(\frac{2}{\alpha} + \frac{\beta^2}{2(1-\alpha)}\right)\langle u, u\rangle + \frac{1}{\beta}\langle S^0 u, u\rangle,$$

and the lower bound 0 comes from non-negativity. Optimizing over α the coefficient in front of $\langle u, u\rangle$, we obtain the greatest possible value of the bound, which we shall call a:

$$a = \frac{2}{\beta} + \frac{\beta}{2} + 2.$$

Therefore, we obtain the following relative bound: Setting $b = 0 \leq \frac{1}{\beta} < 1$, we have

$$0 \leq \langle S^1 u, u\rangle \leq a\langle u, u\rangle + b\langle S^0 u, u\rangle, \quad a = 0 \leq 2b + \frac{1}{2b} + 2. \tag{5.1}$$

Now, we can use (2.15), where, because S^1 is symmetric, we can let $c = 0, \varepsilon = 1$. We must find the proper integration contour around E_0. We can let Γ be a circle on $\mathbb{C}$ in (2.10). The radius that will then maximize ρ_0 is a number that minimizes the norm of the resolvent, which is determined by the midpoint on the real line between E_0, E_1 as determined by (4.3). From this, we get

$$\frac{1}{\rho_0} = \left|\frac{a + bE_0}{z - E_0}\right| = \left|\frac{a + bE_1}{z - E_1}\right|.$$

Using the values for $E_0 = -2, E_1 = -\frac{5}{4}$ we get

$$z_0 = -\frac{13a - 20b}{8a - 13b}$$

which then gives us

$$\rho_0 = \frac{3}{3b + 4b^{-1} + 16}.$$

The value of b that maximizes ρ_0 is $b = \sqrt{2/3}$, giving us

$$\rho_0 = |\kappa| = \frac{1}{7.64}.$$

This yields $Z \approx 7.64$, far above the desired $Z = 2$ value.

5.2. **Kato's refinement.** This is clearly not good enough, so we admit a refinement in which we modify our perturbation to include the entire potential energy, that is, all of the electron interaction terms

$$S^0_\gamma = -\Delta_1 - \Delta_2 - (1-\gamma)\left(\frac{1}{|x_1|} + \frac{1}{|x_2|}\right), \quad 0 < \gamma < 1 \tag{5.2}$$

$$S^1_\gamma = -\gamma\left(\frac{1}{|x_1|} + \frac{1}{|x_2|}\right) + \frac{1}{Z}\frac{1}{|x_1 - x_2|}. \tag{5.3}$$

Unfortunately, S^1_γ is no longer a positive definite operator, so we cannot assume coercivity. However, we can use the positive definiteness of the interaction term and (1.26) to determine that

$$\langle (S^0_\gamma + \beta S^1_\gamma)u, u\rangle \geq -(1-\gamma+\beta\gamma)^2\langle u, u\rangle \tag{5.4}$$

$$\implies -\langle S^1 u, u\rangle \leq \frac{1}{\beta}(1-\gamma+\beta\gamma)^2\langle u, u\rangle + \langle \frac{1}{\beta} S^0 u, u\rangle. \tag{5.5}$$

Therefore, S^0_γ is coercive. We then copy the strategy of the first section: with

$$\begin{aligned} S^0_\gamma = &\left(-\alpha\Delta_1 - (1-\gamma-\beta\gamma)\frac{1}{|x_1|}\right) + \left(-\alpha\Delta_2 - (1-\gamma-\beta\gamma)\frac{1}{|x_2|}\right) \\ &+ \left[-(1-\alpha)(\Delta_1 + \Delta_2) - \frac{1}{|x_1 - x_2|}\right], \end{aligned}$$

we have

$$\langle S^1_\gamma u, u\rangle \leq \left[\frac{2(1-\gamma-\beta\gamma)^2}{\alpha\beta} + \frac{\beta}{2(1-\alpha)Z^2}\right](u, u) + \frac{1}{\beta}\langle S^0_\gamma u, u\rangle.$$

We again minimize the coefficient of the first term on the right with respect to varying α. The result is $\frac{2}{\beta}(1-\gamma-\beta\gamma+\frac{\beta}{2Z})^2$. For convenience, we set $\gamma = \frac{1}{4Z}$. This gives us

$$|\langle S^1_\gamma u, u\rangle| \leq a\langle u, u\rangle + b\langle S^0_\gamma u, u\rangle,$$

where $b = 0 \leq \frac{1}{\beta} < 1$ and

$$a = 0 \leq 2b\left(1 - \frac{1}{4Z} + \frac{1}{4Zb}\right)^2, \quad b \geq \frac{\gamma}{1-\gamma} = \frac{1}{4Z-1}.$$

It is also important to mention that to avoid any complex numbers from appearing, we want

$$1 - \gamma - \beta\gamma \geq 0.$$

Using our value of b, we get

$$b \geq \frac{\gamma}{1-\gamma} = \frac{1}{4Z-1}.$$

Before we find the radius of convergence, we use Theorem 1.26 to determine that the energy levels of S^0_γ have now become

$$-(1-\gamma)\left(1+\frac{1}{(n+1)^2}\right),$$

meaning $E_{\gamma 0} = -2(1-\gamma)$, $E_{\gamma 1} = -\frac{5}{4}(1-\gamma)$.

Therefore, the radius of convergence instead becomes

$$\rho_0 = 3\left(\frac{8a}{(1-\gamma)^2} - 13b\right)^{-1} = \frac{3}{b}\left[\frac{16\left(1-\frac{1}{4Z}+\frac{1}{4Zb}\right)^2}{\left(1-\frac{1}{4Z}\right)^2} - 13\right]^{-1}.$$

If we maximize with respect to b, we obtain

$$b = \frac{1}{\sqrt{3}\left(Z-\frac{1}{4}\right)} > \frac{1}{4Z-1}.$$

Therefore, we obtain the better estimate for ρ_0,

$$\rho_0 = \frac{3\left(Z-\frac{1}{4}\right)}{8+2\sqrt{3}} = \frac{2Z-\frac{1}{2}}{7.64} \implies Z > 4.1. \tag{5.6}$$

$Z > 4.1$ is an improvement of the previous result, which already covers the case of B^{3+}. However, some more effort is needed for the case of the helium atom.

5.3. **Ahlrichs' refinement.** To improve on Kato's bound, Ahlrichs employs a similar scaling argument. However, instead of giving a general scalar and comparison operator, he uses a physically inspired explicit scaling [1]:

$$Z - \sigma > 0$$

where $\sigma > 0$ is called the "screening constant". While Z in the original Schrödinger operator was a scalar that represented the increased strength of the coulomb interaction due to the extra atom in the nucleus, σ represents the relative weakening of the nuclear Coulomb interaction because of the counteraction of the nearby electron-Coulomb interaction.

Let $\nu = (Z-\sigma)^{-1}$. Noting that

$$Z = \frac{1+\sigma\nu}{\nu},$$

we define the scaled operator

$$S(\nu) := \left(\frac{1+\sigma\nu}{\nu}\right)^2\left[S^0 + \frac{\nu}{1+\sigma\nu}S^1\right].$$

Relating the new coefficient on S^1 with the old perturbation parameter κ we obtain:

$$\kappa = \frac{\nu}{1+\sigma\nu} \implies \nu = \frac{\kappa}{1-\sigma\kappa}. \tag{5.7}$$

Therefore, the new ν Schrödinger operator becomes:

$$S_\nu(\kappa,\sigma) = \left(\frac{\kappa}{1-\sigma\kappa}\right)^2\left[S^0 + \frac{1}{\nu}S^1\right]. \tag{5.8}$$

We relate the perturbation parameter with the radius of convergence:

$$\left|\frac{\kappa}{1-\sigma\kappa}\right| < \rho.$$

Finally, this gives us the modified radius of convergence:

$$|\kappa| < \frac{\rho}{1+\sigma\rho} = \rho(\sigma). \tag{5.9}$$

To compute ρ, Ahlrichs derives:

$$\rho = \frac{\beta|E_0 - E_1|}{2E(\beta) + E_0 + E_1} \tag{5.10}$$

where $E(\beta) = \max(E_+(\beta), E_-(\beta))$ is the maximum lower bound of $S_\pm(\beta)$. Ahlrichs' derivation of $E_-(\beta)$ resembles Kato's procedure, deriving $E_-(\beta) = (1 + \frac{1}{4}\sqrt{3}\beta)^2$. More importantly, Ahlrichs corrects the computation of $E_+(\beta)$ that we have been using, (4.5), with an approximation to finite dimensions via a method pioneered by Bazley [3].

5.4. **The Bazley Approximation.** This only works for positive definite perturbations, so for now we return to βS^1 for $\beta > 0$. We are going to find an infinite dimensional basis (necessarily orthogonal) $p_1, p_2, \dots \in L^2$, and we then define P^k to be the projection operator to the linear span of $p_1, \cdots, p_k$ term. We can then define

$$S^k = S_0 + \beta S^1 P^k.$$

If we let E_0^k be the ground state of S^k, then we can use the logic of (4.5) and the non-negativity of βS^1, to get

$$\langle S^0 x, x\rangle \le \langle S^k x, x\rangle \le \langle S^{k+1} x, x\rangle \le \langle S(\kappa) x, x\rangle \tag{5.11}$$

$$E_0^0 \le E_0^k \le E_0^{k+1} \le E_+(\beta). \tag{5.12}$$

Now, take Ψ^k to be an arbitrary eigenvector of S^k such that

$$S^k \Psi^k = E\Psi^k.$$

Through S^k, we give a much sharper bound of the perturbation H by solving a finite-dimensional linear algebra problem.

5.4.1. *Solutions to S^k.* We continue by eliminating anything that is still infinite dimensional. We begin by noting that:

$$\beta S^1 P^k \Psi^k = \sum_{i=1}^{k} c_i \beta S^1 p_i \tag{5.13}$$

$$c_i = \sum_{j=1}^{k} b_{ji} \langle \beta S^1 \Psi^k, p_j\rangle, \quad 1 \le i \le k, \tag{5.14}$$

where (b_{ji}) is the matrix inverse of the one with elements $\langle \beta S^1 p_j, p_i\rangle$.

Next, we define the basis vectors p_i by

$$\beta S^1 p_i = \Psi_i^0, \quad i = 1, 2, \dots, k, \tag{5.15}$$

where each Ψ_i^0 is the eigenstate corresponding to the ith S^0 energy level. Since S^1 is non-negative, we can use Corollary 1.27 to define an inverse operator $(S^1)^{-1}$ satisfying (1.28) such that:

$$p_i = \frac{1}{\beta}(S^1)^{-1}\Psi_i^0, \quad i = 1, \dots, k \tag{5.16}$$

Finally we let Ψ_t^0 be an eigenstate of S^k that was not constructed using (5.15). This forces $\beta S^1 P^k \Psi_t^0 = 0$. This suggests that:

$$S^k \Psi_t^0 = S^0 \Psi_t^0 = E_t^0 \Psi_t^0. \tag{5.17}$$

Therefore, Ψ_t^0 is still a valid eigenvector of S^k. This suggests an eigenvalue of S^0 is similarly an eigenvalue of S^k. By linear dependance, we restrict to eigenvectors ψ_s^0 we can express as:

$$\Psi_s^0 = \sum_i^k \alpha_i \Psi_i^0 \tag{5.18}$$

where Ψ_i^0 is defined as in (5.16).

Combining (5.13), (5.16), (5.17), and (5.18), S^k becomes:

$$S^k \Psi_s^0 = S^0 \Psi_s^0 + \beta S^1 P^k \Psi_s^0 = E \Psi_s^0 \tag{5.19}$$

$$S^0 \sum_{i=1}^k \alpha_i \Psi_i^0 + \beta S^1 P^k \left(\sum_{i=1}^k \alpha_i \Psi_i^0 \right) - E \sum_{i=1}^k \alpha_t \Psi_i^0 = 0 \tag{5.20}$$

$$\sum_{i=1}^k \alpha_i (S^0 \Psi_i^0) + \sum_{i=1}^k \alpha_i \left(\beta S^1 P^k \Psi_i^0 \right) - E \sum_{i=1}^k \alpha_i \Psi_i^0 = 0 \tag{5.21}$$

$$\sum_{i=1}^k \alpha_i E_i^0 \Psi_i^0 + \sum_{j=1}^k \sum_{i=1}^k \alpha_i b_{ij} \Psi_j^0 - E \sum_{i=1}^k \alpha_i \Psi_i^0 = 0. \tag{5.22}$$

The linear independence of ψ_i^0 reduces the above equation to

$$\sum_{i=1}^k \left\{ [E_i^0 - E] \delta_{ij} + b_{ij} \right\} \alpha_i^{(s)} = 0, \quad 1 \le j \le k,$$

where δ_{ij} is the Kronecker delta. Hence, k eigenfunctions and energy levels of S^k are found by the roots of the determinant equation E for $i, j = 1$ where:

$$b_{ij} = \frac{1}{\beta} \langle \Psi_i, \left(S^1\right)^{-1} \Psi_j \rangle.$$

We cite Bazley's calculations of b_{ij} in Appendix A of [3]. $E_+(\beta)$ is then the minimum eigenvalue E calculated with other values of γ in 0.1 step intervals as in table II in [1].

5.5. **Linear Interpolation.** Because (5.9) is a strictly increasing function in ρ, it suffices to maximize (5.10). Since we already know E_0, E_1, we only need to find the exact $\beta, E(\beta)$ that maximize the equation. By definition, self-adjoint operators are linear. Therefore, the sesquilinear form of S_+ is an affine function such that via Theorem 1.26,

$$E_+(\beta) = \inf_\beta \langle S_+(\beta) u, u \rangle$$

where $S_+(\beta) := S^0 + \beta S^1$, is a concave function. Moreover, $E(\beta)$ as in (5.10) is also concave. Therefore, performing a piecewise linear interpolation on the interval $[\beta_0, \beta_M]$ would be a lower bound for $E(\beta)$. We define

$$E_{\text{lin}}(\beta) = \sum_{m=0}^{M-1} \left[\frac{E_m(\beta_{m+1} - \beta) + E_{m+1}(\beta - \beta_m)}{\beta_{m+1} - \beta_m} \right] \mathbb{1}_{\{\beta_m, \beta_{m+1}\}}(\beta),$$

where (β_m, E_m) form an input and an output in a Bazley computation. While we continue to work with β, we note that we would need to scale the energy according to (5.8), if (5.10) were not purely expressed by the energy, meaning the scaling cancels out.

We then fix σ and optimize (5.10) as our objective function before finally optimizing over σ. Doing so gives us

$$\sigma = 0.34, \quad \beta = 1.75.$$

Inserting these values yields the following result

$$\rho(\sigma) = 0.608.$$

This gives us

$$Z > Z_0 = 1.98.$$

Finally, using Ahlrichs' final refinement with Bazley's approximation, we have proved that the perturbation S^1 converges for the helium atom case $Z = 2$. This is not the current optimal bound, as Baker & Freund derived $Z_0 \approx 0.90$ [2], covering every possible physical regime, including the H^- case. Unfortunately, we left out the fact that this analysis only works for the Parahelium case, where the spatial coordinates are symmetric and the total spin of the system is equal to 0. Ahlrichs attempted to apply his methods to the Orthohelium case, where the total spin is 1 and the spatial coordinates are antisymmetric, calculating an unideal bound of $Z_0 \approx 24.6$. Otherwise, Orthohelium is currently unexplored. Nevertheless, it is thanks to the efforts of Kato we know a nonzero radius of convergence ρ_0 exists for this case.

Remark 5.23. It is important to take a step back from the math and consider what this math actually means *physically*. helium is known to be the most stable and unreactive element–so much so that the freezing temperature of helium is absolute zero itself. Given this, we should intuitively imagine that the energy described by the Hamiltonian should reflect this by being well-behaved. The ground state energy not converging implies that the atom does not have enough energy to bind the electrons, resulting in a return to scattering states; if the perturbation of the two-electron problem diverges, we should take this as a consideration that our methods can be improved. The exercise we saw over the past chapter is this very mindset executed in practice.

6. Acknowledgments

I want to thank Peter May and Ewain Gwynne for the opportunity to participate once more in the UChicago Mathematics REU. I want to thank my mentor, Chenyang Shao, who provided excellent guidance from the very beginning of the project, even when abroad in France and China. I would like to thank Tara Ford for providing me with a Metcalf scholarship to undertake this project. Lastly, I want to thank my parents, who took excellent care of me while I was back home in New Jersey.

References

[1] Reinhart Ahlrichs. "Lower bounds for eigenvalues with application to the helium atom". In: *The Journal of Chemical Physics* 39.2 (1963), pp. 614–622.

[2] Jonathan D. Baker et al. "Radius of convergence and analytic behavior of the 1/Z expansion". In: *Phys. Rev. A* 41.3 (Feb. 1990), pp. 1247–1273. DOI: 10.1103/PhysRevA.41.1247.

[3] Norman W. Bazley. "Lower Bounds for Eigenvalues with Application to the Helium Atom". In: *Physical Review* 120.1 (Oct. 1960), pp. 1–12. DOI: 10.1103/PhysRev.120.1.

[4] Aden Chen. *Spectral Theory and the Min-Max Theorem*. REU Paper. University of Chicago Mathematics REU, Sept. 2024. URL: https://math.uchicago.edu/~may/REU2024/REUPapers/Chen,Aden.pdf.

[5] David J. Griffiths and Darrell F. Schroeter. *Introduction to Quantum Mechanics*. Third edition. Cambridge ; New York, NY: Cambridge University Press, 2018. ISBN: 978-1-107-18963-8.

[6] Tosio Kato. *Perturbation Theory for Linear Operators*. 2nd. Classics in Mathematics. Springer, 1995. ISBN: 978-3-540-58661-6. DOI: 10.1007/978-3-642-66282-9.

[7] Peter D. Lax. *Functional Analysis*. Pure and Applied Mathematics: A Wiley Series of Texts, Monographs and Tracts. Wiley-Interscience, 2002. ISBN: 978-0471556046. DOI: 10.1002/0471266983.

[8] Franz Rellich. "Störungstheorie der Spektralzerlegung. I." In: *Mathematische Annalen* 113.1 (1937), pp. 600–619. DOI: 10.1007/BF01449874.

[9] *Section 7: The Kato–Rellich Theorem*. /mnt/data/section7katorellich.pdf. Course/lecture notes, accessed 2025-08-22.