Non-relativistic Matter and Quantized Radiation

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Abstract

This is a didactic review of spectral and dynamical properties of atoms and molecules at energies below the ionization threshold, the focus being on recent work in which the author was involved. As far as possible, the results are described using a simple model with one electron only, and with scalar bosons. The main ideas are explained but no complete proofs are given. The full-fledged standard model of non-relativistic QED and various of its aspects are described in the appendix.

1 Introduction

An atom or molecule in an excited state with energy below the ionization threshold will eventually relax to its ground state by dissipating excess energy in the form of radiation. This process of relaxation to the ground state is one of the basic phenomena responsible for the production of all visible light. It involves a range of energies within a few electron volts; a scale where the electron-positron pair creation and the production of ultraviolet radiation is highly suppressed. In a first mathematical study of relaxation to the ground state it is therefore reasonable and legitimate to work with a model where the electron-positron pair creation is entirely neglected and an ultraviolet cutoff is imposed on the electron-photon interaction. These simplifying assumptions lead to a mathematically well defined model of matter, often called standard-model of non-relativistic quantum electrodynamics, or Pauli-Fierz model. Since the numerical predictions of this model are in good agreement with measurement data it is a viable physical model. Yet, only little mathematically rigorous work on this model had been done before the middle of the 1990s, when several groups of researchers started to investigate various of its aspects. Most influential, perhaps, were the papers of Hübner and Spohn \[33, 34, 35\] on spectral and scattering theory, of Bach et al. on spectral analysis \[7, 9, 10\], of Dereziński and Gérard on scattering theory \[14, 15\], and of Jakšić and Pillet on thermal relaxation \[37, 38, 39, 40\]. The present article reviews recent work on the phenomenon of relaxation to the ground state for

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states with total energy below the threshold energy for ionization. It is guided by papers of Lieb, Loss and Griesemer, and of Fröhlich, Schlein and Griesemer [25, 24, 17, 18]. The focus is on the existence of an ionization threshold and the localization of the electrons below this energy, the existence of a ground state, and the existence and completeness of many-photon scattering states (asymptotic completeness of Rayleigh scattering).

The results to be discussed on existence of a ground state and on the localization of photons with energy below the ionization threshold, unlike previous results, hold for all values of the physical parameters such as the fine structure constant and the ultraviolet cutoff. This is crucial for moving on to physically more realistic models without ultraviolet regularization. The analysis of electron-photon scattering is based on methods and ideas from the scattering theory of $N$-body quantum systems [50, 23, 54, 22]. On the one hand the electron-photon dynamics is easier to analyze than the full $N$-body problem since there is no photon-photon interaction. On the other hand the number of photons is not constant! In fact, it might even diverge as time $t \to \infty$. This divergence is avoided by imposing a cutoff on the interaction between electrons and low-energy photons (infrared-cutoff). It is one of the main open challenges in the mathematical analysis of matter interacting with quantized radiation to prove asymptotic completeness for Rayleigh scattering without this infrared-cutoff.

This article is organized as follows. In Section 2.1 we begin with the description of a simple, but non-trivial model of matter and radiation. There is only one electron, besides the static nuclei, and the radiation is described by scalar bosons.

Sections 2.4, 2.5, 2.7, and 2.8 describe the main results of the papers [24, 25, 17] and [18], respectively. Sections 2.2 and 2.3 summarize mathematical and physical background, and Sections 2.9 and 2.10 are devoted to side issues in the aforementioned papers.

Section 3 outlines the modification of results and proofs that are necessary to accommodate $N > 1$ electrons, and Section 4 ends this review with concluding remarks and a discussion of selected open problems.

There is a self-contained appendix on the standard model of non-relativistic QED.

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2 Matter and Radiation

All electrons of an atom or molecule are well localized near the nuclei if the total energy is below the ionization threshold. Therefore the number of electrons is inessential for the phenomena
to be described mathematically in this section. To simplify notation and presentation we restrict ourselves to one-electron systems; the generalization to \( N > 1 \) electrons is described in Section 3.

2.1 A Simple Mathematical Model

The main features of quantum electrodynamics that are responsible for the phenomena to be studied, are the peculiar form of interaction between light and matter, through creation and annihilation of photons, and the fact that photons are massless relativistic particles. The spin of the electron and the helicity of the photons do not play an essential role in most of our analysis. For the purpose of this introduction we therefore neglect these subtleties and present a caricature of QED which only retains the aforementioned main features. The full-fledged standard model is described in the appendix.

We first introduce our models for matter and radiation separately before describing the composed system and the interaction.

A (pure) state of a quantum particle, henceforth called electron, is described by a normalized vector \( \psi \in L^2(\mathbb{R}^3, \mathbb{C}) \), \( \int_A |\psi(x)|^2 dx \) being the probability to find the particle in the region \( A \subset \mathbb{R}^3 \). Its time evolution is generated by a Schrödinger operator

\[
H_{\text{at}} = -\Delta + V
\]

where \( -\Delta \) is the positive Laplacian and \( V \) is the operator of multiplication with a real-valued function \( V(x), x \in \mathbb{R}^3 \). We assume that \( V \in L^2_{\text{loc}}(\mathbb{R}^3) \) and that there exist constants \( \alpha < 1 \) and \( \beta \) such that

\[
\langle \varphi, V_- \varphi \rangle \leq \alpha \langle \varphi, (\Delta) \varphi \rangle + \beta \langle \varphi, \varphi \rangle
\]

for all \( \varphi \in C^\infty_0(\mathbb{R}^3) \), where \( V_- = \text{max}(-V, 0) \). Hence the operator \( -\Delta + V \) is symmetric and bounded from below, which allows us to define a self-adjoint Hamiltonian \( H_{\text{at}} \) by the Friedrichs’ extension of \( -\Delta + V \).

We shall be most interested in the case where

\[
V(x) = V_Z(x) := -\sum_{j=1}^K \frac{Z_j}{|x - R_j|},
\]

\( Z_j, j = 1 \ldots K, \) are positive integers, and \( R_j \in \mathbb{R}^3 \). The function \( V_Z \) is the potential energy (or the scalar potential in Coulomb gauge) of one electron at \( x \in \mathbb{R}^3 \) in the field of \( K \) nuclei with positions \( R_1, \ldots, R_K \) and atomic numbers \( Z_1, \ldots, Z_K \).

The Hamiltonian \( H_{\text{at}} \) with \( V \) given by \( V_Z \) describes a molecule with one electron and static nuclei in units where the unit of length is \( \hbar^2/(2me^2) = r_B/2 \) and the unit of energy is \( 2e^2/r_B = 4 \text{ Ry} \) (see Appendix A). Here \( r_B = \hbar^2/(me^2) \) is the Bohr radius, \( -e \) is the charge of
the electron and \( m \) is its mass. This Hamiltonian is self-adjoint with domain \( D(H_{\text{at}}) = H^2(\mathbb{R}^3) \), the Sobolev space of twice weakly differentiable \( L^2 \)-functions \[ 11 \, 17 \].

A pure state of the radiation field is described by a normalized vector in the bosonic Fock space over \( L^2(\mathbb{R}^3) \). This is the space

\[
\mathcal{F} = \bigoplus_{n \geq 0} S_n L^2(\mathbb{R}^{3n}; \mathbb{C})
\]

where \( S_0 L^2(\mathbb{R}^0) := \mathbb{C} \), and \( S_n \) denotes the orthogonal projection onto the subspace of square integrable functions \( f(k_1, \ldots, k_n) \) that are symmetric with respect to permutations of the \( n \) arguments \( k_1, \ldots, k_n \in \mathbb{R}^3 \). Such a function describes a state of \( n \) bosons, henceforth called photons, with wave vectors \( k_1, \ldots, k_n \). The vector \(|\text{vac}\rangle = (1, 0, 0, \ldots) \in \mathcal{F} \) is called the vacuum vector. With \( \mathcal{F}_{\text{fin}} \) we denote the subspace of sequences \( \varphi = (\varphi_{n \geq 0}) \in \mathcal{F} \) with \( \varphi_n = 0 \) for all but finitely many \( n \in \mathbb{N} \).

The energy of a state \( \varphi = (\varphi_n)_{n=0}^\infty \in \mathcal{F} \) is measured by the Hamiltonian \( H_f \) defined by

\[
(H_f \varphi)_0 = 0
\]

\[
(H_f \varphi)_n(k_1, \ldots, k_n) = \sum_{j=1}^n \omega(k_j) \varphi_n(k_1, \ldots, k_n), \quad n \geq 1,
\]

where \( \omega(k) = |k| \). The domain of \( H_f \) is the largest set of vectors for which \( 4 \) defines a vector in \( \mathcal{F} \).

The interaction between photons and electrons comes about in a process of creation and annihilation of photons. To describe it mathematically, creation and annihilation operators are needed. Given \( h \in L^2(\mathbb{R}^3) \) and \( \varphi \in \mathcal{F}_{\text{fin}} \) we define \( a^\ast(h) \varphi \) by

\[
[a^\ast(h) \varphi]_n = \sqrt{n} S_n (h \otimes \varphi_{n-1}).
\]

The operator \( a^\ast(h) \) is called a creation operator. It adds a photon with wave function \( h \) to the state \( \varphi \). The annihilation operator \( a(h) \) is the adjoint of the closure of \( a^\ast(h) \). These operators satisfy the canonical commutation relations

\[
[a(g), a^\ast(h)] = (g, h), \quad [a^2(g), a^\ast(h)] = 0.
\]

A further important operator on \( \mathcal{F} \) is the number operator \( N_f \), defined by

\[
(N_f \varphi)_n = n \varphi_n
\]

and \( D(N_f) = \{ \varphi \in \mathcal{F} : \sum n^2 \| \varphi_n \|^2 \} < \infty \).

A state of the composed system of electron and photons is described by a vector \( \Psi \in \mathcal{H}_{\text{at}} \otimes \mathcal{F} \), that is, by a sequence \( (\psi_n)_{n=0}^\infty \) where \( \psi_n \) is a square integrable function

\[
\psi_n(x, k_1, \ldots, k_n),
\]
describing a state of one electron and \( n \) photons. It is often helpful to use that \( \mathcal{H}_{\text{at}} \otimes \mathcal{F} \simeq L^2(\mathbb{R}^3; \mathcal{F}) \) and to consider \( \Psi \) as a square integrable function \( x \mapsto \Psi(x) \) with values in \( \mathcal{F} \). Then \( ||\Psi(x)||_\mathcal{F}^2 \) is the probability density for finding the electron at position \( x \in \mathbb{R}^3 \).

For the generator of the time-evolution \( t \mapsto \Psi_t \) we choose the Hamiltonian

\[
H \equiv H_g = H_{\text{at}} \otimes 1 + 1 \otimes H_f + gH_{\text{int}},
\]

the interaction \( H_{\text{int}} \) being given by

\[
(H_{\text{int}} \Psi)(x) = [a(G_x) + a^*(G_x)] \Psi(x)
\]

\[
G_x(k) = e^{-i k \cdot x} \kappa(k),
\]

where \( g \in \mathbb{R} \) and \( \kappa \in C^\infty_0(\mathbb{R}^3) \). It is easy to prove that \( H_{\text{int}} \) is operator-bounded with respect to \( H_{g=0} \) with bound zero, and hence, for every \( g \in \mathbb{R} \), \( H_g \) is bounded below and self-adjoint on the domain of \( H_{g=0} \) by the Kato-Rellich theorem [47].

Both \( g \) and \( \kappa \) measure the strength of interaction between electron and photons. Given \( \kappa \), some of the results in the following sections hold for \( |g| \) small enough only, others for small \( |g| \neq 0 \). The value \( \kappa(k) \) of the form-factor \( \kappa \) measures the strength of interaction between electron and radiation with wave vector \( k \). There is no interaction for \( k \) outside the support of \( \kappa \), which is the case, e.g., for \( |k| \) larger than the ultraviolet cutoff \( \Lambda := \sup\{|k| : \kappa(k) \neq 0\} \).

We reiterate that this model is a caricature of the standard model of quantum electrodynamics for atoms and molecules interacting with quantized radiation. With QED it has in common that it describes a non-relativistic particle, the electron, interacting with massless relativistic bosons in a momentum conserving process of creation and annihilation of such bosons.

It would make our toy model physically more realistic if we assumed \( \kappa(k) \sim |k|^{-1/2} \) for small \( |k| \). But then \( H \) has no ground state [44], a problem that does not occur in the standard model of non-relativistic QED. Therefore we assume that \( \kappa \) is non-singular near \( k = 0 \).

### 2.2 Spectrum and Eigenfunctions of \( \mathcal{H}_{\text{at}} \)

As a preparation for the following sections we recall a few facts concerning the spectrum of Schrödinger operators \( \mathcal{H}_{\text{at}} = -\Delta + V \) and the decay of their eigenfunctions.

Suppose that \( V \) satisfies assumption (2) and let \( \mathcal{H}_{\text{at}} \) be defined in terms of the Friedrichs’ extension of the symmetric operator \(-\Delta + V \) on \( C^\infty_0(\mathbb{R}^3) \). Let \( D_R = C^\infty_0(|x| > R) \), the space of smooth, compactly supported functions with support outside the ball \( B_R(0) \), and let

\[
\Sigma_{\text{at}} := \lim_{R \to \infty} \left( \inf_{\varphi \in D_R, ||\varphi||=1} \langle \varphi, \mathcal{H}_{\text{at}} \varphi \rangle \right). \tag{7}
\]
By a theorem due to Arne Persson \[46, 2\]

$$\Sigma_{at} = \inf \sigma_{ess}(H_{at})$$  \hspace{1cm} (8)

where $\sigma_{ess}(H_{at})$ denote the essential spectrum of $H_{at}$, i.e. the complement, within the spectrum, of the isolated eigenvalues of finite multiplicity. For the Coulomb potential \[43\], $V_Z(x) \to 0$ as $|x| \to \infty$ and hence $\Sigma_{at} = 0$. Furthermore $\sigma_{ess}(H_{at}) = [0, \infty)$, and by a simple variational argument, $H_{at}$ has infinitely many eigenvalues below 0 \[48\].

Eigenfunctions of $H_{at}$ with energy below $\Sigma_{at}$ decay exponentially with increasing $|x|$: for every eigenvalue $E < \Sigma_{at}$ and every $\beta > 0$ with $E + \beta^2 < \Sigma_{at}$ there exists a constant $C_{\beta}$ such that

$$|\psi(x)| \leq C_{\beta}e^{-\beta|x|}, \quad \text{a.e. on } \mathbb{R}^3$$  \hspace{1cm} (9)

for all normalized eigenfunctions that belong to $E$. Of course, the actual decay of $\psi$ will not be isotropic unless $V$ is spherically symmetric. There is the better, but non-explicit, bound $|\psi(x)| \leq C_\varepsilon e^{-(1-/v)\rho(x)}$ where $\rho(x)$ is the geodesic distance from $x$ to the origin with respect to a certain metric $ds^2 = c_E(x/|x|)dx^2$ in $\mathbb{R}^3$ \[2\]. Since $c_E(x/|x|) \geq \Sigma_{at} - E$ (if $\Sigma_{at} < \infty$), the isotropic bound (9) follows from this stronger result.

For proving (9) it suffices to show that

$$e^{\beta|x|}\psi \in L^2(\mathbb{R}^3)$$  \hspace{1cm} (10)

whenever $E + \beta^2 < \inf \sigma_{ess}(H_{at})$. The point-wise bound (10) then follows from a general result on point-wise bounds for (weak) solutions of second order elliptic equations \[2\] \[21\]. The $L^2$-bound (10), in turn, is easily derived from the characterization \[7\] \[8\] for $\inf \sigma_{ess}(H_{at})$ \[36\].

We now turn again to $H_g$, the Hamiltonian \[5\] describing matter and radiation. Most properties of $H_g$ to be discussed in the following sections hold for all $g \in \mathbb{R}$, including $g = 0$. Hence they generalize properties of

$$H_{g=0} = H_{at} \otimes 1 + 1 \otimes H_f.$$  

By general spectral theory $\sigma(H_0) = \sigma(H_{at}) + \sigma(H_f)$. Furthermore, it is easy to see from the definition of $H_f$ that $\sigma(H_f) = [0, \infty)$ and that 0 is the only eigenvalue of $H_f$, the vacuum $|\text{vac}\rangle$ being its eigenvector. It follows that $\sigma(H_0) = [\inf \sigma(H_{at}), \infty)$ and that $H_0$ and $H_{at}$ have the same eigenvalues. The corresponding eigenvectors are the products $\psi \otimes |\text{vac}\rangle$, where $\psi$ is an eigenvector of $H_{at}$.

2.3 Physical Phenomena and Mathematical Description

The experimental evidence on isolated atoms in contact with radiation is easiest described in an idealized setup or “Gedankenexperiment”. Consider an atom in a universe that is otherwise
free of matter. For simplicity, we assume that the atom has only one electron. There may be radiation near the atom initially but no “external fields” or sources of radiation shall be present. Independent of its initial state, this system of atom and radiation will eventually approach one of only two qualitatively distinct final states: the “bound state” or the “ionized state”.

In the bound state the atom is in its ground state, the state of least energy, where the electron is confined to within a small neighborhood of the nucleus. All excess energy has been radiated off. This radiation is very far away from the atom and escaping at the speed of light.

In the ionized state the electron and the nucleus are spatially separated with increasing distance. In addition, there may be radiation going off to infinity.

Of course, the ionized state can only be attained if the total energy of matter and radiation initially is high enough to overcome the attraction between nucleus and electron. High energy however, does not guarantee ionization, as the excess energy may just as well turn into radiation. On the other hand, if the total energy initially is not sufficient for ionization, then the atom will certainly relax to its ground state. Other conceivable scenarios, like relaxation to a stationary state with non-minimal energy, or the permanent radiation without total loss of the excess energy have never been observed. Bohr’s stationary states, with the exception of the ground state, are unstable, and radiation is only emitted in the very short period of transition to the ground state.

The goal is to give a proof of the phenomenon of relaxation to the ground state in the model introduced in the previous section. In view of the experimental evidence described above, we expect that this model has the following mathematical properties.

**Existence of the ionization threshold.** There exists a threshold energy \( \Sigma \geq \inf \sigma(H) \), such that the electrons described by states in the spectral subspace \( E_{(-\infty,\Sigma)}(H)\mathcal{H} \) are well localized near the nuclei, while states with energy above \( \Sigma \) may be ionized.

**Existence of a ground state.** There exists a state of least energy (ground state), or, equivalently, \( \inf \sigma(H) \) is an eigenvalue of \( H \).

**Absence of excited stationary states.** The operator \( H \) has no eigenvalues above \( \inf \sigma(H) \).

**Asymptotic completeness of Rayleigh scattering (ACR).** In the limit \( t \to \infty \) the time evolution \( e^{-iHt}\Psi \) of every state \( \Psi \in E_{(-\infty,\Sigma)}(H)\mathcal{H} \) is well approximated by a superposition of states of the form

\[
a^*(h_{1,t}) \cdots a^*(h_{n,t}) e^{-iE_0t}\Psi_0,
\]

where \( h_{i,t}(k) = e^{-i|k|t} h_i(k) \), \( \Psi_0 \) is a normalized ground state of \( H \) and \( E_0 \) is its energy. The vector \( \Psi \) describes a state composed of the atom in its ground state and \( n \) freely
propagating photons with wave functions $h_{1,t}, \ldots, h_{n,t}$. In the limit $t \to \infty$ they will be far away from the atom.

The papers [24, 25, 17, 18] are devoted to proving the above four properties for the standard model of QED was well as for the model introduced in Section 2.1. One exception is asymptotic completeness for Rayleigh scattering where the results concern the model of Section 2.1 only, with the additional important simplification that $\kappa(k) = 0$ for $|k| \leq \sigma$ where $\sigma > 0$ is arbitrarily small but positive. This assumptions that photons with energy near zero don’t interact with the electron is usually referred to as an infrared cutoff, IR-cutoff, for short. Sometimes the constant $\sigma$ is called infrared cutoff as well. The significance of the IR-cutoff is that it allows us to control the number of bosons that are being produced in the course of time: the number of bosons with energy below $\sigma$ stays constant and the number of bosons with energy above $\sigma$ can be bounded from above in terms of the total energy. The assumption of an IR-cutoff is not expected to be necessary for the validity of asymptotic completeness of Rayleigh scattering as formulated above; but as of now, no convincing mathematical argument is known that would substantiate this believe.

The above list of physical phenomena is limited to the coarsest properties of atoms interacting with radiation. Even below the ionization threshold, there are many other phenomena that are worth rediscovering in the standard model, and in part this has already been done. Most important, perhaps, are the occurrence of sharp lines in the spectrum of the emitted radiation (Bohr frequencies), the resonances in lieu of Bohr’s stationary state and their extended life time, and the correspondence principle at energies near the ionization threshold. We shall come back to some of these phenomena in later sections, when we review known results or comment on open problems. One must keep in mind, however, the limitations of our model. Quantitative predictions will be of limited accuracy when relativity or high-energy photons play a significant role.

### 2.4 Exponential Decay and Ionization Threshold

The ionization threshold $\Sigma$ of an atom or molecule with only one electron is the least energy that this system can achieve in a state where the electron has been moved “infinitely far away” from the nuclei. The electron is outside the ball $|x| < R$ with probability one, if its wave function $\Psi(x)$ vanishes in this ball. Therefore we define

$$\Sigma = \lim_{R \to \infty} \inf_{\Psi \in D_R, \|\Psi\|=1} \langle \Psi, H \Psi \rangle$$

(12)

where

$$D_R = \{ \Psi \in D(H) | \Psi(x) = 0 \text{ if } |x| < R \}.$$
Note the analogy with Persson’s characterization \((7)\) of \(\inf\sigma_{ess}(H_{at})\). Here, however, \(\Sigma \neq \inf\sigma_{ess}(H)\) unless \(\Sigma = \inf\sigma(H)\). In general \(\Sigma \geq \inf\sigma(H)\) and, if \(V(x) \to 0\) as \(|x| \to \infty\), then \(\Sigma = \inf\sigma(H - V)\), which is greater than \(\inf\sigma(H)\) for \(V = V_Z\) \([25]\) (see also Section \(2.5\)).

According to \((12)\), the electron described by a state \(\Psi\) with energy below \(\Sigma\) cannot be arbitrarily far away from the origin. In fact, by \([24]\), for all \(\lambda, \beta \in \mathbb{R}\) with \(\lambda + \beta^2 < \Sigma\)

\[
\|((e^{\beta|x|} \otimes 1)E_\lambda(H))\| < \infty. \tag{13}
\]

This shows that the probability(-density) \(\|\Psi(x)\|_F^2\) to find the electron at the point \(x\) decays exponentially fast, as \(|x| \to \infty\), at least in the averaged sense

\[
\int e^{2\beta|x|}\|\Psi(x)\|_F^2 \, dx < \infty. \tag{14}
\]

There is an obvious similarity between \((14)\) and \((10)\) that is not accidental. In \([24]\) the bound \((13)\) is derived from an abstract result for semi-bounded self-adjoint operators \(H\) in Hilbert spaces of the form \(L^2(\mathbb{R}^n) \otimes \mathcal{F}\), where \(\mathcal{F}\) is an arbitrary complex Hilbert space. The only assumptions are that \(f \mathcal{D}(|H|^{1/2}) \subset \mathcal{D}(|H|^{1/2})\) and that

\[
f^2H + Hf^2 - 2fHf = -2|\nabla f|^2 \tag{15}
\]

for smooth, bounded functions \(f(x)\) with bounded first derivatives. Equation \((15)\) holds for \(H = -\Delta \otimes 1\) and since the left-hand side of \((15)\) formally equals \([f, [f, H]]\), it follows that \((15)\) holds for any large class of self-adjoint operators \(H\) whose principal symbol is given by the Laplacian. The result \((10)\) thus emerges as a special case of \((13)\).

Even though the above assumptions on \(H\) are largely independent of \(H_f\) and \(gH_{int}\), the result depends on these operators! The binding energy \(\Sigma - \inf\sigma(H)\) depends of \(g\) and hence so does the decay rate one obtains for the ground state.

It is well known, since the work of Agmon \([2]\), that eigenfunctions of second order elliptic equations decay exponentially in energetically forbidden regions, that is, in regions where the differential operator, as a quadratic form, is strictly larger than the eigenvalue \([2]\). The result \((13)\) shows that this idea can be brought to bear in a much more general framework, including many models of non-relativistic QED. It is clear that our proof of \((13)\) can be generalized, along the lines of \([2]\), to yield non-isotropic bounds, as well as exponential bounds for QED-models where \(H_{at}\) is a more general, uniformly elliptic second order differential operator.

We owe the strategy for proving \((13)\) to Bach et al. \([7]\), where this bound is established for \(|g|\) sufficiently small and \(\lambda + \beta^2 < \Sigma_{at} - \text{const}|g|\).

### 2.5 Existence of a Ground State

By the main result of \([25]\), \(\inf\sigma(H)\) is an eigenvalue of \(H\) whenever

\[
\inf\sigma(H) < \Sigma. \tag{16}
\]
This reduces a difficult spectral problem to a variational problem: the problem of finding a state $\Psi \in D(H)$ with $\langle \Psi, H\Psi \rangle < \Sigma \langle \Psi, \Psi \rangle$. There are two important classes of potentials $V$ for which this variational problem can be solved without much effort: if $V(x) \to \infty$ as $|x| \to \infty$, then obviously $\Sigma = \infty$ and hence $\inf \sigma(H) < \Sigma$. On the other hand, if $V(x) \to 0$ as $|x| \to \infty$ then $\Sigma = \inf \sigma(H-V)$ where the nuclei are removed in $H-V$. Using the translation invariance of $H-V$ one shows that

$$\inf \sigma(H) \leq \inf \sigma(H-V) + \inf \sigma(-\Delta + V).$$

It follows that $\inf \sigma(H) < \Sigma$ whenever $V(x) \to 0$, $(|x| \to \infty)$ and $\inf \sigma(-\Delta + V) < 0$. Since this is the case for the Coulomb potential $V = V_Z$, all one-electron atoms and molecules have a ground state.

We next sketch the proof that (16) guarantees existence of a ground state. To begin with we recall that a hypothetical eigenvector $\Psi$ of $H$, with eigenvalue $\inf \sigma(H)$, minimizes the quadratic form $\Psi \mapsto \langle \Psi, H\Psi \rangle$ subject to the constraint $\|\Psi\| = 1$. It is thus natural to establish existence of $\Psi$ by proving relative compactness for a suitable minimizing sequence. The problem with this approach is that a generic minimizing sequence will tend weakly to zero. The fact that $\inf \sigma(H)$ belongs to the essential spectrum alone implies that there are infinitely many energy minimizing sequences with this defect. Our task is thus, first, to choose a suitable minimizing sequence, and second, to prove its relative compactness.

We choose the elements of our minimizing sequence to be the ground states $\Psi_m$ of modified Hamiltonians $H_m$ ($m \to 0$) in which the photon energy $\omega(k)$ is altered to be $\omega_m(k) = \sqrt{k^2 + m^2}$. That is, we give the photons a positive mass $m$. For $m$ small enough the binding assumption (16) is inherited by $H_m$, which we use to show that $\inf \sigma(H_m)$ is indeed an eigenvalue. As a matter of fact, $\inf \sigma(H_m)$ is separated from the essential spectrum of $H_m$ by a gap of size $m$ [15]. The sequence of ground states $(\Psi_m)_{m>0}$ is a minimizing sequence for $H$ that can be assumed to be weakly convergent. It remains to show that the weak limit is not the zero vector in $H$.

We first argue that it suffices to prove relative compactness of the sequence of $L^2$-functions $\psi_{m,n}(x, k_1, \ldots, k_n)$ restricted to large balls $B \subset \mathbb{R}^{(3+3n)}$. This follows from the exponential decay w.r.t. to $x$, from $\psi_{m,n}(x, k_1, \ldots, k_n) = 0$ if $|k_i| > \Lambda$, and from the bound $\sup_m \langle \Psi_m, N_f \Psi_m \rangle < \infty$. Then we use the compactness of the embedding

$$W^{1,p}(B) \hookrightarrow L^2(B), \quad \text{for } 2 > p > \frac{2 \cdot (3 + 3n)}{2 + (3 + 3n)}$$

due to Rellich-Kondrachov [1]. We thus need to show that $\sup_m \|\nabla \psi_{m,n}\|_p < \infty$, which we derive from a refinement of the argument that we used to prove the bound on $\langle \Psi_m, N_f \Psi_m \rangle$, and from the $H$-boundedness of $-\Delta_x$. 

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There was a large number of previous papers on the existence of a ground state for models similar to the one discussed here [4, 5, 7, 9, 19, 30, 31, 52]. Among these, the best result is due to Bach et al [9]. It established existence of a ground state when $\inf \sigma(H_{\text{at},N})$ is an isolated eigenvalue and the fine-structure constant $\alpha$ is small enough. Most importantly, in this paper for the first time existence of a ground state is proven in the standard model without an IR-regularization.

2.6 Relaxation to the Ground State is a Scattering Phenomenon

As discussed in Section 2.3, every state $\Psi \in \text{Ran}(H)$ is expected to “relax to the ground state by emission of photons”. In mathematical terms, this means that $e^{-iHt}\Psi$, in the distant future, $t \to \infty$, is well approximated in norm by a linear combination of vectors of the form

$$a^*(h_{1,t}) \ldots a^*(h_{n,t})e^{-iE_0t}\Psi_0$$  \hspace{1cm} (17)

where $h_{i,t}(k) = e^{-i\omega t}h_i(k)$, $\Psi_0$ is the ground state, and $E_0$ is its energy. This has a chance to be correct only if $H$ has no other eigenvalues below $\Sigma$. If it has, then relaxation to a bound state may occur, which means that $\Psi_0$ in (17) may be any eigenvector of $H$ with eigenvalue below $\Sigma$. In this weaker form, the above assertion is called Asymptotic Completeness for Rayleigh scattering. The problem of proving absence of excited eigenvalues is independent of the scattering problem and its discussion is deferred to a later section.

Before proving completeness of the scattering states one needs to address the problem of their existence. An example of a scattering state is a vector $\Psi_+ \in \mathcal{H}$ for which there exist $n \geq 1$ photons $h_1, \ldots, h_n$ and an eigenvector $\Psi$, $H\Psi = E\Psi$ such that

$$e^{-iHt}\Psi_+ \simeq a^*(h_{1,t}) \ldots a^*(h_{n,t})e^{-iEt}\Psi, \hspace{1cm} t \to \infty$$

in the sense that norm of the difference vanishes in the limit $t \to \infty$. The scattering state $\Psi_+$ is said to exists if the limit

$$\Psi_+ = \lim_{t \to \infty} e^{iHt}a^*(h_{1,t}) \ldots a^*(h_{n,t})e^{-iEt}\Psi \hspace{1cm} t \to \infty$$  \hspace{1cm} (18)

exists. Let $\mathcal{H}_+$ denote the closure of the space spanned by vectors $\Psi_+$ of the form (18). All elements of $\mathcal{H}_+$ are called scattering states and asymptotic completeness of Rayleigh scattering is the property that

$$\mathcal{H}_+ \supset \text{Ran}(H).$$  \hspace{1cm} (19)

Existence of scattering states is established in [17], and [19] is proven in [18] for the model introduced in Section 2.1 assuming either an infrared cutoff on the interaction or that the photon dispersions relation $\omega(k)$ is bounded from below by a positive constant, which excludes $\omega(k) = |k|$. The latter assumption serves the same purpose as the infrared cutoff, and it is
satisfied, e.g., for massive bosons where \( \omega(k) = \sqrt{k^2 + m^2} \) with \( m > 0 \). As of today, there is no proof of (19) without a form of infrared cutoff or another drastically simplifying assumption [3, 51].

2.7 Existence of Scattering States

Generalizing (18), we ask whether the limits

\[
\Psi_+ = \lim_{t \to \infty} \psi^{iHt} \alpha^\#(h_{1, t}) \ldots \alpha^\#(h_{n, t}) e^{-iHt} \psi
\]

exist for given \( \psi \in \mathcal{H} \), and \( h_t \in L^2(\mathbb{R}^3) \), where \( \alpha^\#(h_{i, t}) \) is a creation or an annihilation operator. The scattering states \( \Psi_- \) obtained in the limit \( t \to -\infty \) are physically interesting as well, but the problem of their existence is mathematically equivalent to the existence of (20). Beginning with the easiest case, \( n = 1 \), let us ask whether the limits

\[
a_+^\#(h) \psi = \lim_{t \to \infty} \psi^{iHt} \alpha^\#(h_t) e^{-iHt} \psi
\]

exist. If the photons are massless, as they are in nature, the answer depends on the electron dispersion relation and on the energy distribution of \( \psi \). For massive photons, however, \( a_+^\#(h) \psi \) exists for all \( \psi \in D(\mathcal{H}) \) and all \( h \in C^0(\mathbb{R}^3) \), and the proof is short and easy [32]: by the Cauchy criterion the limit (21) exists if the time derivative of the right-hand side is (absolutely) integrable. A straightforward computation using \( a^\star(h_t) = e^{-iHt} a^\#(h_t) e^{iHt} \) and (5) shows that

\[
\int_1^\infty \left\| \frac{d}{dt} e^{iHt} a^\star(h_t) e^{-iHt} \psi \right\| dt = \int_1^\infty \left\| (G_x, h_t) e^{-iHt} \psi \right\| dt
\]

where

\[
(G_x, h_t) = \int e^{ik \cdot x - i\omega_t(k) h(k)} dk
\]

and \( \omega(k) = \sqrt{k^2 + m^2} \). Since the Hessian of \( \omega \) is strictly positive,

\[
\sup_x |(G_x, h_t)| \leq \text{const} \ t^{-3/2}, \quad t \geq 1
\]

by a standard result on oscillatory integrals [49]. Hence \( \|(G_x, h_t) e^{-iHt} \psi \| \leq \text{const} \ t^{-3/2} \) and (21) is finite which proves the existence of \( a_+^\#(h) \psi \). For massless photons, however,

\[
\sup_x |(G_x, h_t)| \sim \text{const} \ t^{-1}, \quad t \geq 1
\]

which is not integrable and we need to estimate the integrand of (22) more carefully. To begin with, we note that the phase in (23) is non-stationary away from the “wave front” \( |x| = t \). Hence

\[
\sup_{x: ||x||/t - 1 \geq \epsilon} |(G_x, h_t)| \leq \frac{C_n}{t^n}, \quad t \geq 1
\]
for every integer \( n \), and it remains to estimate
\[
\int_0^\infty \frac{dt}{t} \left\| \chi_{[1-\varepsilon,1+\varepsilon]}(|x|/t)e^{-iHt}\Psi \right\|.
\] (24)

Finiteness of (24) requires, in particular, that the electrons do not propagate at the speed of light, which is true in nature, but not precluded for the dynamics generated by the non-relativistic Schrödinger operator \( H_{\text{el}} \). The easiest case occurs when the electrons are in a bound state \( \Psi \in \text{Ran}E_\lambda(H) \), \( \lambda < \Sigma \), where, by (13),
\[
\sup_t \left\| e^{\beta|x|}e^{-iHt}\Psi \right\| \leq \left\| e^{\beta|x|}E_\lambda(H) \right\| < \infty
\] (25)
for some \( \beta > 0 \). Then obviously the integrand in (24) decays exponentially in time, and hence the limit (21) exists. If \( \Psi \) is not in a bound state but its energy is insufficient for an electron to reach the speed \( 1 - \varepsilon \), then (24) is still finite, at least if \( H \) is the Hamiltonian (37) of the standard model [17]. More precisely, (24) is finite for all \( \Psi \) in a dense subspace of \( \text{Ran}E_\lambda(H) \) with \( \lambda < \Sigma + m/2 \), and for \( \varepsilon \) in (24) small enough. Here \( m/2 = mc^2/2 \) is the non-relativistic kinetic energy of a particle at the speed of light. The assumption \( \lambda < \Sigma + m/2 \) thus ensures that no electron can reach the speed of light.

The asymptotic field operators have the important property that
\[
a^+_\ast(g)\text{Ran}E_\lambda(H) \subset \text{Ran}E_{\lambda+M}(H)
\]
\[
a_+(h)\text{Ran}E_\lambda(H) \subset \text{Ran}E_{\lambda-m}(H)
\] (26)
if \( \text{supp}(g) \subset \{k : |k| \leq M\} \) and \( \text{supp}(h) \subset \{k : |k| \geq m\} \). Using (26) and the existence of the limit (21) we prove existence of the limit (20) and that
\[
\lim_{t \to \infty} e^{iHt}a^\#(h_{1,t}) \ldots a^\#(h_{n,t})e^{-iHt}\Psi = a^\#(h_1) \ldots a^\#(h_n)\Psi
\] (27)
if \( \psi \in \text{Ran}E_\lambda(H) \), \( \lambda + \sum_j M_j < \Sigma \), where \( M_j = \text{sup}\{|k| : h_j(k) \neq 0\} \) and the sum \( \sum_j M_j \) extends over all creation operators in (27). The main technical difficulty in this last step is the unboundedness of the asymptotic field operators (21).

From the above discussion it is clear that it is physically more sensible to describe the time evolution of the electron by a relativistic Hamiltonian such as
\[
H_{\text{rel}} = \sqrt{-\Delta + 1} + V(X),
\] (28)
in place of (11). Then (24) is finite for all \( \Psi \) in any spectral subspace \( E_\lambda(H)\mathcal{H} \) with \( \lambda < \infty \). Hence the asymptotic operators \( a^\#_+(h) \) exist on a dense subspace of \( \mathcal{H} \). The main results in [17, 18, 16] apply to both electron-Hamiltonian, (11) and (28).

To conclude this discussion of scattering states we remark that for Rayleigh scattering it suffices to prove existence of the asymptotic field-operators \( a^\#_+(h) \) on \( \text{Ran}E_{(-\infty,\Sigma)}(H) \), which follows from (25). The improved results discussed thereafter are important in the study of photon scattering at a free electron (Compton scattering) [16].
2.8 Asymptotic Completeness

A characterization of ACR that is mathematically more convenient than (19) is achieved by mapping the freely propagating photons $h_{i,t}$ in (18) into an auxiliary Fock space $\mathcal{F}$. We attach $\mathcal{F}$ to the Hilbert space $\mathcal{H}$ by defining an extended Hilbert space $\tilde{\mathcal{H}} = \mathcal{H} \otimes \mathcal{F}$. The appropriate time evolution on $\tilde{\mathcal{H}}$ is generated by the extended Hamiltonian $\tilde{H} = H \otimes 1 + 1 \otimes H_f$. Furthermore, we define an identification operator $I : D \subset \tilde{\mathcal{H}} \to \mathcal{H}$ on a dense subspace $D$ of $\tilde{\mathcal{H}}$ by

$$I \Psi \otimes |\text{vac}\rangle = \Psi$$

and linear extension. Since $e^{-iH_ft}|\text{vac}\rangle = |\text{vac}\rangle$ and $a^*\left(h_{i,t}\right)e^{-iH_ft}a^*\left(h\right)e^{iH_ft}$ we can use $I$ to write

$$a^*(h_{1,t}) \cdots a^*(h_{n,t})e^{-iH_t}\Psi = Ie^{-i\tilde{H}_t}\left[\Psi \otimes a^*(h_1) \cdots a^*(h_n)|\text{vac}\rangle\right].$$

If $\Psi$ is an eigenvector of $H$ and $P_B$ denotes the orthogonal projection onto the closure of the span of all eigenvectors, it follows that

$$a^*_+(h_1) \cdots a^*_+(h_n)\Psi = \lim_{t \to \infty} e^{i\tilde{H}_t}a^*(h_{1,t}) \cdots a^*(h_{n,t})e^{-iH_t}\Psi$$

$$= \Omega_+ \left[\Psi \otimes a^*(h_1) \cdots a^*(h_n)|\text{vac}\rangle\right]$$

where

$$\Omega_+ = s - \lim_{t \to \infty} e^{i\tilde{H}_t}Ie^{-i\tilde{H}_t}P_B \otimes 1$$

is the wave operator. Thus existence of scattering states becomes equivalent to existence of the wave operator $\Omega_+$, and, since $\text{Ran}\Omega_+ = \mathcal{H}_+$, asymptotic completeness as defined in (19) becomes

$$E_{(-\infty,\Sigma)}(H) \subset \text{Ran}\Omega_+.$$  \hfill (29)  

(It turns out that $\Omega_+$ is a partial isometry and hence $\text{Ran}\Omega_+$ is closed.)

The reader familiar with quantum mechanical scattering theory is cautioned not to think of ACR as a form of asymptotic completeness for potential scattering. The comparison dynamics generated by $\tilde{H}$ is not the free dynamics for all bosons. The bosons in the first factor of $\tilde{H}$ still fully interact with the electrons. Rayleigh scattering is more similar to $N$-body quantum scattering with the additional complication that the number of particles is fluctuating.

Asymptotic completeness of Rayleigh scattering, as described in Section 2.6 makes two assertions. First, any initial state $\Psi \in \text{Ran}E_{(-\infty,\Sigma)}(H)$, that is not an eigenvector of $H$, in the course of time will relax to a bound state by emission of photons. Second, the asymptotic dynamics of the emitted radiation is well approximated by the free photon dynamics. Our proof of ACR contains two main technical ingredients that address these issues. In both of them we need to assume that either the photons are massive, i.e., $\omega(k) = \sqrt{k^2 + m^2}$, or that
an infrared cutoff $\sigma > 0$ is imposed on the interaction. In the second case $m = \sigma/2$ in the following.

Our first main ingredient is an estimate on the ballistic spatial expansion of the system for states with energy distribution away from $S = \sigma_{pp}(H) + \mathbb{N}m$. We show that $S$ is closed and countable and that for each $\lambda \in \mathbb{R}\setminus S$ there is an open interval $\Delta \ni \lambda$ and a positive constant $C_\lambda$ such that
\[
\langle \Psi_t, d\Gamma(y^2)\Psi_t \rangle \geq C_\lambda t^2, \quad t \to \infty
\]
for all $\Psi \subset \text{Ran}E_\Delta(H)$. The proof is based on the positivity of the commutator obtained by differentiating the left hand side twice with respect to time. This positive commutator estimate, often called Mourre estimate, is proven by induction in energy steps of size $m$ along a strategy very similar to the proof of the Mourre estimate for $N$-body Schrödinger operators [36]. We generalize the Mourre estimate in [14] to accommodate our model.

The second main ingredient is a propagation estimate for the asymptotic dynamics of escaping photons. Explicitly we show that
\[
\int_1^\infty dt \langle \Psi_t, fF\Gamma(P_t)Ff\Psi_t \rangle \leq C\|\Psi\|^2
\]
for all $\Psi \in \mathcal{H}$, where
\[
P_t = (\nabla \omega - y/t) \cdot \chi(|y| \geq t^{\delta})(\nabla \omega - y/t)
\]
and $0 < \delta < 1$. Here $f$ is an energy cutoff, $F = F(d\Gamma(y^2/t^2\lambda^2))$ a space cutoff, and $\lambda > 0$ a parameter that is chosen sufficiently large eventually. The left-hand side of (31) compares the average photon velocity, $y/t$, with the group velocity, $\nabla \omega$, for photons in the region $\{|y| \geq t^\delta\}$. This includes all photons that escape the electron ballistically. The finiteness of $C$ thus confirms that the dynamics of outgoing radiation is approaching the free photon dynamics in the limit $t \to \infty$.

Asymptotic completeness had previously been established for a model with $\Sigma = \infty$ (confined electrons), and massive photons $\omega(k) = \sqrt{k^2 + m^2}$, $m > 0$, by Dereziński and Gérard [14]. The methods in [14] could probably be extended to prove ACR for our system. Instead of doing so, we chose to give an entirely new proof of AC based on the relatively elementary propagation estimate (31), and using (30) as the only dynamical consequence of the Mourre estimate. Our work is inspired by the Graf-Schenker proof of asymptotic completeness for $N$-body quantum systems [22].

2.9 Absence of Excited States

At present the knowledge on absence of eigenvalues above $\inf \sigma(H_g)$ is far less complete then, e.g., our knowledge regarding existence of a ground state. Known results on absence of eigenvalues are derived under the assumption that $g > 0$ is small enough [7, 8, 10, 15], and to ensure
that no new eigenvalues emerge near $\inf \sigma(H)$ an infrared cutoff is imposed \[18\]. There is a further assumption, the Fermi golden rule condition, which ensures that eigenvalues of $H_{g=0}$ dissolve for $g \neq 0$. This assumption can be checked in any explicitly given model.

For the model introduced in Section 2.1, with the assumption of an infrared cutoff, the following results hold true. For any given $\varepsilon > 0$ and for $|g| > 0$ small enough, depending on $\varepsilon$, 

$$\sigma_{pp}(H_{g}) \cap (\inf \sigma(H_{g}), \Sigma_{at} - \varepsilon) = \emptyset,$$

where $\Sigma_{at} = \inf \sigma(H_{at})$ \[10, 18\]. This result, combined with ACR from the previous section implies that $\text{Ran} \Omega_{+} \supset \text{Ran} E(\inf \sigma(H), \Sigma_{at} - \varepsilon) (H)$ where the projector $P_B$ in the definition of $\Omega_{+}$ is the projector onto the ground state. That is, every $\psi \in \text{Ran} E(\inf \sigma(H), \Sigma_{at} - \varepsilon) (H)$ relaxes to the ground state in the sense of Section 2.6, (17).

It has been asserted in \[8\] that the methods of \[7, 10\] can be used to show absolute continuity of the spectrum of $H$ above and away from $\Sigma_{at}$ for small $|g|$. This is presumably correct but a proof is missing.

The strategy for proving absence of eigenvalues in a given spectral interval $\Delta \subset \mathbb{R}$ is clear and simple: One tries to find a symmetric operator $A$ on $\mathcal{H}$, such that

$$E_{\Delta}(H)[iH,A]E_{\Delta}(H) \geq CE_{\Delta}(H)$$

with a positive constant $C$. Since, formally, $\langle \Psi, [iH,A] \Psi \rangle = 0$ for every eigenvector $\Psi$ of $H$, it immediately follows that $\sigma_{pp}(H) \cap \Delta = \emptyset$. The main problems, of course, are to find a suitable conjugate operator $A$, and to make these formal arguments rigorous.

### 2.10 Relaxation to the Ground State

An important consequence of AC for Rayleigh scattering and the absence of eigenvectors besides a unique ground state $\Psi_{0}$, is relaxation to the ground state. To explain this let $\mathcal{A}$ denote the $C^{*}$-algebra generated by all operators of the form

$$B \otimes e^{i\phi(h)}, \quad B \in \mathcal{L}(\mathcal{H}_{at}), \quad h \in C_{0}^{\infty}(\mathbb{R}^{3}),$$

where $\phi(h) = a(h) + a^{*}(h)$. We say that $\Psi_{t} = e^{-iHt} \Psi$ relaxes to the ground state $\Psi_{0}$, if

$$\lim_{t \to \infty} \langle \Psi_{t}, A \Psi_{t} \rangle = \langle \Psi_{0}, A \Psi_{0} \rangle \langle \Psi, \Psi \rangle \quad (32)$$

for all $A \in \mathcal{A}$. Suppose $H$ has a unique ground state $\Psi_{0}$ and let $\mathcal{H}_{+}$ denote the space of scattering states over $\Psi_{0}$. That is, $\mathcal{H}_{+}$ is the closure of the span of all vectors of the form

$$a^{*}_{+}(h_{1}) \cdots a^{*}_{+}(h_{n}) \Psi_{0}.$$
Then, by a short computation, all states in $\mathcal{H}_+$ relax to the ground state $\Psi_0^{17}$. Since the assumptions of Section 2.9 imply AC in the form

$$\mathcal{H}_+ \supset \text{Ran} E_{(\inf \sigma(H), \Sigma_{at}-\varepsilon)}(H_g)$$

for given $\varepsilon > 0$ and small enough coupling $|g|$, it follows that all state in $\text{Ran} E_{(\inf \sigma(H), \Sigma_{at}-\varepsilon)}(H_g)$ relax to the ground state in the sense of Equation 32.

3 N-Electron Atoms and Molecules

We now briefly describe how the results of the previous sections are generalized to the case of $N > 1$ electrons. For simplicity we neglect spin and Pauli principle. A (pure) state of $N$ electrons is described by a vector $\psi \in L^2(\mathbb{R}^{3N})$, and the Schrödinger operator for $N$ electrons in the field of $K$ static nuclei is given by

$$H_{at,N} = \sum_{j=1}^{N} (-\Delta x_j + V_Z(x_j)) + \sum_{i<j} \frac{1}{|x_i - x_j|}$$

where $x_j \in \mathbb{R}^3$ is the position of the $j$th electron. The coupling of the electrons to the radiation field is done by a straightforward generalization of (6). The Hamiltonian of the entire system is given by

$$H_{g,N} = H_{at,N} \otimes 1 + 1 \otimes H_f + gH_{\text{int}}$$

$$H_{\text{int}} = \sum_{j=1}^{N} [a(G_{x_j}) + a^*(G_{x_j})], \quad G_{x_j}(k) = e^{-ik \cdot x_j} \kappa(k)$$

and acts on $L^2(\mathbb{R}^{3N}) \otimes \mathcal{F}$. Again, $H_g$ is self-adjoint on $D(H_{g=0})$.

3.0.1 Spectrum and eigenfunctions of $H_{at,N}$

Like $H_{at}$, $H_{at,N}$ is a Schrödinger operator of the general form $-\Delta + V$, and hence $\inf \sigma_{ess}(H_{at,N})$ is given by Persson’s theorem:

$$\inf \sigma_{ess}(H_{at,N}) = \lim_{R \to \infty} \left( \inf_{R \in \mathcal{D}_R, \|\varphi\|=1} \langle \varphi, H_{at,N,\varphi} \rangle \right) =: \Sigma_{at,N}$$

where $\mathcal{D}_R = C_c^\infty(|X| > R)$. Using the decay of the two-body potentials and the electron-electron repulsion one shows that $\Sigma_{at,N} = \inf \sigma(H_{at,N-1})$, which leads to

$$\inf \sigma_{ess}(H_{at,N}) = \inf \sigma(H_{at,N-1}), \quad (33)$$

a special case of the more general HVZ-Theorem $^{48, 36}$. For $Z > N - 1$ the system described by $H_{at,N-1}$ has a net positive charge and can bind at least one more electron. It follows,
by a simple variational argument, that \( \inf \sigma(H_{at,N}) < \inf \sigma(H_{at,N-1}) \), which, by (33) implies that \( \inf \sigma(H_{at,N}) \) is an eigenvalue of \( H_{at,N} \). In fact, \( H_{at,N} \) has infinitely many (discrete) eigenvalues below \( \inf \sigma_{ess}(H_{at,N}) \) [43]. The continuous part of the spectrum of \( H_{at,N} \) is the interval \( [\inf \sigma_{ess}(H_{at,N}), \infty) \), and this interval may contain further eigenvalues below 0 [53]. For a discussion of the structure of the continuous spectrum, the reader is referred to [36].

The results (9), (10) on the decay of eigenfunctions hold for Schrödinger operators in arbitrary dimensions, hence in particular for \( H_{at,N} \). Better, non-isotropic exponential bounds are known too, but they are expressed in terms of a geodesic distance \( \rho(X) \) w.r.t to a metric in \( \mathbb{R}^{3N} \) that depends on the spectra of the Hamiltonians \( H_{at,k} \), for \( k < N \) [2, 36]. Explicit expressions for \( \rho \) are known for \( N \leq 3 \), and for atoms under the (unproven) assumption that the ionization energy increases monotonically as the electrons, one by one, are removed from the atom [12].

This concludes our discussion of \( H_{at,N} \) and we return to the composed system of \( N \) electrons and radiation.

### 3.0.2 Exponential decay and ionization thresholds

The ionization threshold \( \Sigma \) is the least energy that an atom or molecule can achieve in a state where one or more electrons have been moved “infinitely far away” from the nuclei. In an \( N \)-particle configuration \( X \in \mathbb{R}^{3N} \), one or more electrons are far away from the (static) nuclei if and only if \( |X| \) is large. In this respect there is no difference between \( N = 1 \) and \( N > 1 \) besides the dimension of the configuration space. Since this dimension is irrelevant for the proof of (13), our result on exponential decay for \( N > 1 \) and its proof are straightforward generalizations of result and proof for \( N = 1 \). Let \( D_R := \{ \Psi \in D(H) | \Psi(X) = 0 \text{ if } |X| < R \} \) and let

\[
\Sigma_N = \lim_{R \to \infty} \left( \inf_{\Psi \in D_R, \|\psi\|=1} \langle \Psi, H_N \Psi \rangle \right).
\]  

(34)

Then for all real numbers \( \lambda \) and \( \beta \) with \( \lambda + \beta^2 < \Sigma \),

\[
\| (e^{\beta|X|} \otimes 1) E_\lambda(H_N) \| < \infty.
\]  

(35)

In the case of only one electron subject to an external potential \( V \) that vanishes at infinity, such as \( V_Z \), we saw that \( \Sigma_{N=1} = \inf \sigma(H_1 - V) \). The proper generalization to \( N > 1 \) is analogous to the HVZ theorem for \( N \)-particle Schrödinger operators. We show that

\[
\Sigma_N = \min_{N' \geq 1} \{ E^V_{N-N'} + E^0_{N'} \}
\]  

(36)

where \( E^0_{N'} \) is the least energy of \( N' \) electrons with no nuclei present, \( Z = 0 \) [24]. Like the HVZ theorem, (36), for the bottom of the essential spectrum of \( H_{at,N} \), equation (36) requires the decay of the interaction between material particles with increasing spacial separation. While
this decay is obvious for the instantaneous Coulomb interaction, it is more tedious to quantify for the interaction mediated through the quantized radiation field. The main problem in proving (36), however, is to control the error which arises when the field energy is split up into two parts, one associated with the \( N' \) electrons far out and one with the other \( N - N' \) electrons. This error is proportional to the number of photons, as measured by the number operator \( N_f \), which in turn is not bounded with respect to the total energy and thus not under control. To deal with this problem we first prove (36) with an IR-cutoff \( \sigma > 0 \) in the interaction and then we show that (36) is obtained in the limit \( \sigma \to 0 \) [25, 24].

The characterization (36) of the ionization threshold is important for proving that \( \Sigma_N > \inf \sigma(H_N) \).

### 3.0.3 Existence of a ground state

The dimension of the electron configuration space is inessential for proving that (16) guarantees existence of a ground state. Therefore \( \inf \sigma(H_N) \) is an eigenvalue of \( H_N \) whenever

\[
\inf \sigma(H_N) < \Sigma_N.
\]

However, it is much harder to verify this condition for \( N > 1 \). The only easy case occurs for spatially confining external potentials where \( \Sigma_N = \infty \). In a tour de force Lieb and Loss recently showed that

\[
E^Z_N < \min_{N' \geq 1} \{ E^Z_{N-N'} + E^0_{N'} \}
\]

for all atoms and molecules with \( Z > N - 1 \) [33]. Combined with (36) this proves that \( E^Z_N < \Sigma_N \) and hence that \( E^Z_N \) is an eigenvalue of \( H^Z_N \) indeed.

### 4 Concluding Remarks and Open Problems

The results we have described on localization of the electron, existence of a ground state and existence of scattering states are established in [24, 25, 17] within the standard model of QED for non-relativistic electrons (see Appendix A). Asymptotic completeness is proved for the dipole approximation of that model, Hamiltonian (59), an approximation that is physically reasonable for confined electrons [18]. We don’t expect serious obstacles in proving ACR for the standard model (with IR cutoff), but to do so appears prohibitive in view of the additional work due to the interaction terms quadratic in creation and annihilation operators. The most important and most interesting open problem in connection with Rayleigh scattering is to prove completeness without IR cutoff. This has been done so far only for the explicitly soluble model of a harmonically bound electron coupled to radiation in dipole approximation [3], and for perturbations thereof [51]. Steps toward ACR for more general electron Hamiltonians have been undertaken by Gérard [20].
The problem of the emitted low energy radiation can be understood as one aspect of the more general question of the intensity of the radiation in Rayleigh scattering as a function of the frequency. Experimentally, sharp spectral lines with frequencies \( \omega \) given by Bohr’s condition are observed. This condition says that \( \hbar \omega \) is the difference between the energies of two stationary states, that is, between two eigenvalues of \( H_{\text{st}} \). From quantum theory this phenomenon is expected to be a consequence of the smallness of \( \alpha \), which allows one to compute transition amplitudes in leading order perturbation theory. Rigorous work in this direction is currently being done by Bach, Fröhlich and Pizzo [6]. One also expects that eigenvalues of \( H_{\text{st}} \) show up as resonances in the spectrum of \( H_g \) and that the eigenvectors of \( H_{g=0} \) are meta-stable states for the dynamics generated by \( H_g \), if \( g > 0 \), with a life-time inversely proportional to the resonance width. Both these expectations have been confirmed by work of Bach et al, and by Mück [9, 45]. While the existence of resonances and meta-stable states is consistent with the experimentally observed spectral lines, it does not fully account for them. It remains to be shown that, for small \( \alpha \), first order transitions between meta-stable states dominate the process of relaxation to the ground state and hence that the intensity is largest for radiation obeying Bohr’s frequency condition. A related question is the one about a confirmation of the correspondence principle within QED. By the correspondence principle, the frequency of radiation emitted by a highly excited atom agrees with the angular frequency of a classical point charge on the corresponding Bohr orbit. This principle together with Bohr’s frequency condition determines the distribution of eigenvalues of highly excited states. A rigorous derivation of the correspondence principle would therefore confirm – but not prove – the domination of Bohr frequencies at least in the low energy spectrum.

Many further questions arise once we allow for total energies above the ionization threshold \( \Sigma \). Then the atom can become ionized and the dynamics of the removed electrons is close to the free one. The first task is thus to study the scattering of photons at a freely moving electron, the so-called Compton scattering. This has been done in [16], where we established asymptotic completeness for Compton scattering for energies below a threshold energy that limits the speed of the electron from above to one-third of the speed of light. To do so, we had to impose an infrared cutoff, for otherwise no dresses one-electron states exist.

The natural next step is to combine Rayleigh with Compton scattering to obtain a complete classification of the long time asymptotics of matter coupled to radiation. This would include the photo effect as well as the occurrence of Bremsstrahlung.

There are also very interesting and difficult open questions related to the binding energy \( \Sigma - E_N \) even for \( N = 1 \). From Section 2.5 we know that

\[
E_{N=1} \leq \Sigma + \inf \sigma(-\Delta + V).
\]

That is, if \( V \to 0 \), the binding energy \( \Sigma - E_{N=1} \) with coupling to the radiation field is at least as
large as the binding energy \(-\inf \sigma(-\Delta + V)\) without radiation. Physical intuition tells us that this binding energy should actually increase due to the coupling to radiation: the radiation field accompanying the electron, by the energy-mass equivalence, adds to the inertia of the electron, that is, makes it heavier and thus easier to bind. This \textit{mass renormalization} can explicitly be computed in the dipole approximation and this has been used to prove enhanced binding by Hiroshima and Spohn [29]. Without dipole approximation the mass renormalization is not known explicitly and enhanced binding has been established so far only for small \(\alpha\) [26, 27]. It is an interesting and challenging problem to establish enhanced binding without dipole approximation and for arbitrary \(\alpha\) and \(\Lambda\).

Once there are two or more electrons, one would like to know, first of all, whether two electrons attract or repel each another in our model of matter. Of course, equal charges repel each other but this argument neglects the effect of the quantized radiation field, which is attractive. Two charges close to each other will share part of their radiation field. Since this reduces the energy to produce it, binding is encouraged. The questions is thus whether this binding effect may overcome the Coulomb repulsion.

\section{Non-relativistic QED of Atoms and Molecules}

The purpose of this appendix is to describe atoms and molecules within UV-regularized, non-relativistic quantum electrodynamics in Coulomb gauge. We shall also comment on suitable choices of units, on representations of the theory that avoid the use of polarization vectors, and on the dipole approximation. For further information the reader is referred to [7, 11, 13].

\subsection{A.1 Formal Description of the Model}

To write down the model quickly and in a form familiar from physics books we shall be somewhat formal at first, using operator-valued distributions and avoiding domain questions.

The Hilbert space of pure states of \(N\) electrons and an arbitrary number of transversal photons is the tensor product \(\mathcal{H} = \mathcal{H}_{\text{at}} \otimes \mathcal{F}\) where

\[
\mathcal{H}_{\text{at}} := \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3; \mathbb{C}^2), \quad \mathcal{F} := \bigoplus_{n=0}^{\infty} \otimes_{s}^{n} L^2(\mathbb{R}^3; \mathbb{C}^2),
\]

\(\otimes_{s}^{n} L^2 := \mathbb{C}\), and where \(\otimes_{s}^{n} L^2(\mathbb{R}^3; \mathbb{C}^2), n \geq 1\), stands for the symmetrized tensor product of \(n\) copies of \(L^2(\mathbb{R}^3; \mathbb{C}^2)\). The vector \(\Omega := (1, 0, 0, \ldots) \in \mathcal{F}\) is called \textit{vacuum}. The one-particle wave functions in \(\mathcal{H}_{\text{at}}\) and \(\mathcal{F}\) are \(\mathbb{C}^2\)-valued to account for the two spin and the two polarization states of the electrons and transversal photons, respectively.

The Hamiltonian of an atom or molecule with static nuclei is a self-adjoint operator in \(\mathcal{H}\)
of the form
\[ H = \sum_{j=1}^{N} \frac{1}{2m} \left[ \sigma_j \cdot (-i \nabla x_j + \sqrt{\alpha} A_\Lambda(x_j)) \right]^2 + \alpha V_R \otimes 1 + 1 \otimes H_f, \]  
(37)
where \( \sigma_j = (\sigma_{j,x}, \sigma_{j,y}, \sigma_{j,z}) \) denotes the triple of Pauli matrices acting on the spin degrees of freedom of the \( j \)th electron and \( x_j \in \mathbb{R}^3 \) is the position of the \( j \)th electron. The constant \( m > 0 \) is the (bare) mass of an electron and \( \alpha = e^2/(\hbar c) = e^2/\hbar c \) is the fine structure constant. In our units \( \hbar = 1 = c \). Another common form of \( H \) is obtained by using that
\[ \left[ \sigma \cdot (-i \nabla x + \sqrt{\alpha} A_\Lambda(x)) \right]^2 = (-i \nabla x + \sqrt{\alpha} A_\Lambda(x))^2 + \sqrt{\alpha} \sigma \cdot B(x) \]  
(38)
where \( B(x) = \text{curl} A(x) \).

The operator \( V_R \) acts by multiplication with the electrostatic potential
\[ V_R(x) = - \sum_{j=1}^{K} \sum_{i=1}^{N} \frac{Z_j}{|x_i - R_j|} + \sum_{i<j} \frac{1}{|x_i - x_j|} \]  
(39)
of the electrons in the field of \( K \) static nuclei with positions \( R_1, \ldots, R_K \in \mathbb{R}^3 \) and atomic numbers \( Z_1, \ldots, Z_K \in \mathbb{Z}_+ \). We use the short-hands \( x = (x_1, \ldots, x_N) \) and \( R = (R_1, \ldots, R_N) \).

The operators \( H_f \) and \( A_\Lambda(x) \), for fixed \( x \in \mathbb{R}^3 \), are operators on Fock space. \( H_f \) has been defined in Section 2.1 and \( A_\Lambda(x) \) can be expressed in the form
\[ A_\Lambda(x) = (2\pi)^{-3/2} \sum_{\lambda=1,2} \int_{|k| \leq \Lambda} \frac{d^3 k}{\sqrt{2|k|}} \left\{ \varepsilon_\lambda(k)^* e^{ik \cdot x} a_\lambda(k) + \varepsilon_\lambda(k) e^{-ik \cdot x} a_\lambda^\dagger(k) \right\}. \]  
(40)
The polarization vectors \( \varepsilon_\lambda(k) \in \mathbb{C}^3 \), \( \lambda \in \{1,2\} \), are orthogonal to the wave vector \( k \) and normalized
\[ \varepsilon_\lambda^\dagger(k) \cdot \varepsilon_\mu^\dagger(k) = \delta_{\lambda\mu}, \quad \varepsilon_\lambda^\dagger(k) \cdot k = 0. \]  
(41)
In addition we assume that \( \varepsilon_\lambda(tk) = \varepsilon_\lambda(k) \) for all \( t > 0 \). The operators \( a_\lambda^\dagger(k) \) and \( a_\lambda(k) \) are creation- and annihilation operators in \( \mathcal{F} \). These are operator-valued distributions, formally defined by \( a_\lambda(k) \Omega = 0 \) for all \( k \in \mathbb{R}^3 \), \( \lambda \in \{1,2\} \), and by the canonical commutation relation
\[ [a_\lambda(k), a_\mu^\dagger(q)] = \delta_{\lambda\mu} \delta(k - q), \quad [a_\lambda^\dagger(k), a_\mu^\dagger(q)] = 0. \]  
(42)
A rigorous definition of \( A_\Lambda(x) \) will be given in the next section. The constant \( \Lambda > 0 \) in (40) is the ultraviolet cutoff. Photons with \( |k| > \Lambda \) do not interact with the electrons under the dynamics generated by \( H \). This is nonphysical but necessary to define \( A_{\Lambda,i}(x) \) on a dense subspace of \( \mathcal{F} \). For \( \Lambda = \infty \) not even the vacuum would be in the domain of \( A(x) \). In fact, by a formal computation using the properties of \( a_\lambda(k) \) and \( a_\lambda^\dagger(k) \), \( \| A_i(x) \Omega \|^2 = \text{const} \int_{|k| \leq \Lambda} |k|^{-1} d^3 k \to \infty \) as \( \Lambda \to \infty \).

In the QED of Feynman, Schwinger and Tomanaga, removing the UV cutoff requires a renormalization of mass, charge and field strength, a procedure that is mathematically not sufficiently well understood yet.
A.2 Atomic Units and Perturbation Theory

To work in the small-\(\alpha\) regime it is convenient to choose the UV-cutoff \(\Lambda\) and the nuclear positions \(R_i \in \mathbb{R}^3\) fixed on scales of energy and length where the units are proportional to the Rydberg energy \(m\alpha^2/2 = mc^2\alpha^2/2\) and the Bohr radius \(1/(m\alpha) = \hbar^2/mc^2\). We shall therefore rewrite the Hamiltonian in these units. It is instructive to begin by first scaling electron position and photon momentum independently. Let \(U : \mathcal{H} \to \mathcal{H}\) be defined by

\[
(U\varphi)_{n}(x, k_1, \ldots, k_n) = \eta^{3/2} \mu^{3n/2} \varphi_n(\eta x, \mu k_1, \ldots, \mu k_n).
\]

Then

\[
\mu^{-1} U H U^* = \sum_{j=1}^{N} \frac{1}{2m\eta^2 \mu} \left[ \sigma_j \cdot (-i \nabla_{x_j} + \sqrt{\alpha \eta \mu} A_{\Lambda}(\eta x_j)) \right]^2 + \frac{\alpha}{\eta \mu} V_R/\eta \otimes 1 + 1 \otimes H_f,
\]

which is most easily verified using the definition of \(A_{\Lambda}(x)\) given in the next section. In order that \(2m\eta^2 \mu = 1\) and \(\eta \mu = \alpha\) we choose \(\eta = (2m\alpha)^{-1}\) and \(\mu = 2m\alpha^2\). Next we express the UV cutoff and the nuclear positions in these units, that is we replace

\[
\Lambda/\mu \to \Lambda, \quad R/\eta \to R,
\]

a non-unitary change of the Hamiltonian! Thus in the new units the Hamiltonian reads

\[
\sum_{i=1}^{N} \left[ \sigma_i \cdot (-i \nabla_i + \alpha^{3/2} A_{\Lambda}(\alpha x_i)) \right]^2 + V_R \otimes 1 + 1 \otimes H_f
\]

where the dependence on \(\alpha\) is concentrated in electron-photon interaction \(\alpha^{3/2} A_{\Lambda}(\alpha x)\). The papers by Bach et al. concern the Hamiltonian \((45)\), many others concern \((37)\). When comparing results that are valid for small \(\alpha\) only, one must keep in mind that these Hamiltonians are not equivalent, not even for atoms: the substitution \(\Lambda \to \Lambda \alpha^2\), which occurs in \((44)\), corresponds to the change \(m \mapsto m/\alpha^2\) of the electron mass, as follows from \((13)\) with \(\eta = \mu^{-1} = \alpha^2\).

A.3 Fock-Spaces, Creation- and Annihilation Operators

We next give a rigorous definition of the quantized vector potential \(A_{\Lambda}(x)\) and we shall comment on the self-adjointness of \(H\). In order to prepare the ground for the next section we define Fock space, creation- and annihilation operators in larger generality then needed here. A good reference for this section is [11].

Given a complex Hilbert space \(\mathfrak{h}\) the bosonic Fock space over \(\mathfrak{h}\),

\[
\mathcal{F} = \mathcal{F}(\mathfrak{h}) = \oplus_{n \geq 0} \mathcal{S}_n(\otimes^n \mathfrak{h})
\]

is the space of sequences \(\varphi = (\varphi_n)_{n \geq 0}\), with \(\varphi_0 \in \mathbb{C}\), \(\varphi_n \in \mathcal{S}_n(\otimes^n \mathfrak{h})\), and \(\sum_{n \geq 0} \|\varphi_n\|^2 < \infty\). Here \(\mathcal{S}_n\) denotes the orthogonal projection onto the subspace of symmetrized tensor products.
of $n$ vectors in $\mathfrak{h}$. The inner product in $\mathcal{F}$ is defined by
\[
\langle \varphi, \psi \rangle = \sum_{n \geq 0} (\varphi_n, \psi_n),
\]
where $(\varphi_n, \psi_n)$ denotes the inner product in $\otimes^n \mathfrak{h}$. We use $\mathcal{F}_{\text{fin}}$ to denote the dense subspace of vectors $\varphi \in \mathcal{F}$ with $\varphi_n = 0$ for all but finitely many $n \in \mathbb{N}$.

Given $h \in \mathfrak{h}$ the creation operator $a^*(h) : \mathcal{F}_{\text{fin}} \subset \mathcal{F} \to \mathcal{F}$ is defined by
\[
[a^*(h)\varphi]_n = \sqrt{n}S_n(h \otimes \varphi_{n-1})
\]
and the annihilation operator $a(h) : \mathcal{F}_{\text{fin}} \subset \mathcal{F} \to \mathcal{F}$ is the restricted to $\mathcal{F}_{\text{fin}}$ of the adjoint of $a^*(h)$. The operators $a(h)$ and $a^*(h)$ satisfy the canonical commutation relations (CCR)
\[
[a(g), a^*(h)] = (g, h), \quad [a^*(g), a(h)] = 0.
\]
In particular, $[a(h), a^*(h)] = \|h\|^2$ which implies that $\|a(h)\varphi\| + \|\varphi\|$ and $\|a^*(h)\varphi\| + \|\varphi\|$ are equivalent norms. It follows that the closures of $a(h)$ and $a^*(h)$ have the same domain. On this domain $a^*(h)$ is the adjoint of $a(h)$ \cite{11} Theorem 5.2.12. The operator
\[
\phi(h) = \frac{1}{\sqrt{2}}(a(h) + a^*(h)) \quad (48)
\]
is essentially self-adjoint on $\mathcal{F}_{\text{fin}}$ \cite{11}. It is useful to note that
\[
[a(g), \phi(h)] = i \text{Im}(g, h).
\]

In the case of QED, $\mathfrak{h} = L^2(\mathbb{R}^3; \mathbb{C}^2)$ with inner product $(g, h) = \sum_{\lambda=1,2} \int g_{\lambda}(k)k \lambda(k) \, dk$ and $A_i(x) = \phi(G_{x,i})$, $G_{x,i} \in \mathfrak{h}$, $i = 1, 2, 3$, being the components of
\[
G_{x}(k, \lambda) = \frac{\kappa(k)}{|k|^3} \mathcal{C}_{\lambda}(k)e^{-ikx},
\]
where $\kappa(k) = (2\pi)^{-3/2} \chi_{|k| \leq \Lambda}(k)$. More generally we may allow $\kappa$ to be any real-valued, spherically symmetric function with $\kappa/\sqrt{\Lambda} \in L^2(\mathbb{R}^3)$. In particular $|\kappa(-k)| = |\kappa(k)|$ which implies that $[A_i(x), A_j(y)] = 0$ for all $x, y \in \mathbb{R}^3$ and $i, j \in \{1, 2, 3\}$.

The Hamiltonian \cite{37} is defined and symmetric on the dense subspace
\[
\mathcal{D} = \bigotimes_{i=1}^{N} C_0^\infty(\mathbb{R}^3; \mathbb{C}^2) \otimes \mathcal{F}_{\text{fin}}(C_0^\infty(\mathbb{R}^3; \mathbb{C}^2))
\]
where $\mathcal{F}_{\text{fin}}(C_0^\infty(\mathbb{R}^3; \mathbb{C}^2))$ is the space of vectors $\varphi = (\varphi_n)_{n \geq 0} \in \mathcal{F}_{\text{fin}}$ with $\varphi_n = \otimes^n C_0^\infty(\mathbb{R}^3; \mathbb{C}^2)$.

Let $H_0 = -\Delta \otimes 1 + 1 \otimes H_f$. Then $H_0$ is essentially self-adjoint on $\mathcal{D}$, self-adjoint on $D(H_0) = D(-\Delta \otimes 1) \cap D(1 \otimes H_f)$, and $H - H_0$ is bounded relative to $H_0$. It follows that the closure of $H' \mathcal{D}$ is defined on $D(H_0)$ and symmetric on this domain. Since $H$ is self-adjoint on $D(H_0)$, according to Hiroshima \cite{28}, we conclude that $H$ is essentially self-adjoint on $\mathcal{D}$. Alternatively, the Hamiltonian \cite{37} may be self-adjointly realized in terms of the Friedrichs’ extension of $H' \mathcal{D}$, since this operator is bounded from below, or, by using the theorem of Kato-Rellich for $\Lambda/\alpha$ small enough \cite{9}. ($\alpha\Lambda$ small enough for the Hamiltonian \cite{15}.)
A.4 Avoiding Polarization Vectors

The fact that the polarization vectors are necessarily discontinuous as functions of \( \hat{k} = k/|k| \in S^2 \), by a well-known result of H. Hopf, may lead to annoying technical problems [25]. To show how these problems can be avoided we construct a representation of \( H \) that does not depend on a choice of polarization vectors [18, 42]. This representation is based on a description of single-photon states by vectors in

\[ h_T := \{ h \in L^2(\mathbb{R}^3; \mathbb{C}^2) | h(k) \cdot k = 0 \ \text{for all} \ k \}, \]

the space of transversal photons. Let \( u : L^2(\mathbb{R}^3; \mathbb{C}^2) \to h_T \) be the unitary map

\[ u : (h_1, h_2) \mapsto \sum_{\lambda=1,2} h_\lambda \varepsilon^*_\lambda \]  

where \( \{ \varepsilon_\lambda \}_{\lambda=1,2} \) are the polarization vectors employed in the definition of \( H \), an let \( U : \mathcal{F} \to \mathcal{F}(h_T) \) be defined by

\[ Ua^*(h)U^* = a^*(uh), \ \ \ \ \ \ \ \ \ \ U\Omega = \Omega. \]

It follows that \( UA_i(x)U^* = \phi(uG_{x,i}) \) where

\[
(uG_{x,j})(k) = \sum_{\lambda=1,2} \frac{\kappa(k)}{|k|^{1/2}} \varepsilon_\lambda(k)_j \varepsilon_\lambda(k)^* \\
= \frac{\kappa(k)}{|k|^{1/2}} e^{-ik \cdot x} (e_j - \hat{k}(\hat{k} \cdot e_j)), \tag{53}
\]

\( \{e_1, e_2, e_3\} \) being the canonical basis of \( \mathbb{R}^3 \). Note that \( \phi(uG_{x,j}) \) is one operator and not a triple of operators even though \( k \mapsto uG_{x,j}(k) \) is a vector-valued function.

The Hamilton operator \( H_T = UHU^* \) is the desired new representation of \( H \). It has the form of \( H \) in [37] with the only difference that the form-factor of \( A(x) \) is now given by (53), a function in \( C^\infty(\mathbb{R}^3 \setminus \{0\}) \).

By choosing other unitary mappings \( u \) from \( L^2(\mathbb{R}^3; \mathbb{C}^2) \) onto \( h_T \) one may define more equivalent representations of QED. For example the map

\[ u_2 : (h_1, h_2) \mapsto \sum_{\lambda=1,2} h_\lambda \varepsilon^*_\lambda \wedge \hat{k} \]  

leads to the representation of \( H \) where the quantized vector potential is defined in terms of the form factor

\[
(u_2G_{x,i})(k) = \frac{\kappa(k)}{|k|^{1/2}} e^{-ik \cdot x} (e_i \wedge \hat{k}), \tag{55}
\]

the choice preferred in [42].

For the mathematical analysis of systems of electrons interacting with photons it is often necessary to localized the photons in their position space. That is, the photon wave function
where \( h \in \mathfrak{h}_T \) is mapped to \( J(i \nabla_k) h \) where \( J \in C_0^\infty(\mathbb{R}^3) \). Now \( J(i \nabla_k) h \not\in \mathfrak{h}_T \) unless \( J = 0 \) or \( h = 0 \), and projecting \( J(i \nabla_k) h \) back to \( \mathfrak{h}_T \) would destroy the localization accomplished by the operator \( J(i \nabla_k) \). The solution to this problem is to work on the enlarged one-boson Hilbert space \( \mathfrak{h}_{ext} = L^2(\mathbb{R}^3; \mathbb{C}^3) = \mathfrak{h}_T \oplus \mathfrak{h}_L \) which also includes the space of longitudinal photons \( \mathfrak{h}_L = \{ h| k \wedge h(k) = 0 \} \). The Hilbert space for the entire system becomes \( \mathcal{H}_{ext} = \mathcal{H}_{at} \otimes \mathcal{F}(\mathfrak{h}) \simeq \mathcal{H} \otimes \mathcal{F}(\mathfrak{h}_L) \) and we define a Hamiltonian on \( \mathcal{H}_{ext} \) by

\[
H_{ext} = H_T \otimes 1 + 1 \otimes H_{f,L} = \sum_{j=1}^{N} \frac{1}{2m} [\sigma_j \cdot (-i \nabla_j + \alpha^{1/2} A(x))]^2 + V_R + H_f
\]

where \( A_j(x) = \phi(uG_{x,j}) \) as above, but now \( uG_{x,j} \) is considered as an element of \( \mathfrak{h}_{ext} = L^2(\mathbb{R}^3; \mathbb{C}^3) \). The fake longitudinal bosons from \( \mathfrak{h}_L \) do not interact with the electrons and hence do not affect the dynamical properties of the system. However, by definition of \( H_{ext} \) they contribute additively to the total energy and need to be projected out at the end of any analysis of the energy spectrum.

To conclude this section we return to a more formal representation of \( A(x) \) by expanding photon wave functions in terms of \( \delta \)-distributions. Let \( \delta_k(q) = \delta(q - k) \). We define, formally,

\[
a_j^\#(k) = a_j^\#(e_j \delta_k), \quad a^\#(k) = (a_1^\#(k), a_2^\#(k), a_3^\#(k)).
\]

From the expansion \( h(k) = \sum_{j=1}^{3} \int h_j(q)e_j \delta_k(q) d^3q \) and the (semi)-linearity of \( a^\#(h) \) we obtain

\[
a(h) = \sum_{j=1}^{3} \int h_j(k)a_j(k) d^3k = \int h(k) \cdot a(k) d^3k
\]

\[
a^*(h) = \sum_{j=1}^{3} \int h_j(k)a_j^*(k) d^3k = \int h(k) \cdot a^*(k) d^3k.
\]

In particular, in the representation defined by (53),

\[
A(x) = \int \frac{\kappa(k)}{|k|^{1/2}} P(k) \{ e^{ik \cdot x} a(k) + e^{-ik \cdot x} a^*(k) \} d^3k
\]

where \( P(k) \) denotes the orthogonal projection onto the plane perpendicular to \( k \). If (54) is used then

\[
A(x) = \int \frac{\kappa(k)}{|k|^{1/2}} \hat{k} \wedge \{ e^{ik \cdot x} a(k) + e^{-ik \cdot x} a^*(k) \} d^3k.
\]

### A.5 The Dipole Approximation

In the dipole approximation of QED the quantized vector potential \( A(x) \) in the Hamiltonian is replaced by \( A(0) \). By (38) the Hamiltonian (37) then reduces to

\[
H_{dip} = \sum_{j=1}^{N} \frac{1}{2m} (-i \nabla_j + \alpha^{1/2} A(0))^2 + \alpha V_R + H_f
\]

(56)
where the interaction with the electron spin has dropped out. Without loss of generality we may now describe the electrons by vectors in the smaller space $\mathcal{H}_{\text{at}} = \wedge_i^N L^2(\mathbb{R}^3)$ of spin-less $N$-fermion systems.

The “constant” vector potential in (56) may be gauged away with the help of the operator-valued gauge transformation

$$U = \exp \left( \alpha^{1/2} \sum_{i=1}^N x_i \cdot A(0) \right),$$

also known as Pauli-Fierz transformation. Since $U(-i\nabla_{x_j})U^* = -i\nabla_{x_j} - \alpha^{1/2}A(0)$, $UA(0)U^* = A(0)$, and

$$UHfU^* = H_f + \sqrt{\alpha} \sum_{j=1}^N x_j \cdot E(0) + \alpha \parallel \kappa \parallel^2 \left( \sum_{j=1}^N x_j \right)^2$$

where $E(0) = -i[H_f, A(0)]$ is the quantized electric field, we arrive at

$$UH_{\text{dip}}U^* = \sum_{j=1}^N \left( -\frac{1}{2m} \Delta x_j + \sqrt{\alpha} x_j \cdot E(0) \right)$$

$$+ \alpha V_R + H_f + \alpha \parallel \kappa \parallel^2 \left( \sum_{j=1}^N x_j \right)^2. \quad (58)$$

The dipole approximation seems justified when all electrons are localized in a small neighborhood of the origin $x = 0$, that is, when the total energy is below the ionization threshold. It then seems equally justified to drop the last term in (58) and to multiply $x \cdot E(0)$ with a space cutoff $g \in C_0^\infty(\mathbb{R}^3)$; the later serves to ensure that the Hamiltonian $H$ remains semi-bounded (after dropping the last term). This leads us to

$$\tilde{H}_{\text{dip}} = \sum_{j=1}^N \left( -\frac{1}{2m} \Delta x_j + \sqrt{\alpha} g(x_j) x_j \cdot E(0) \right) + \alpha V_R + H_f, \quad (59)$$

which is also called dipole approximation of (37). It has the advantage, over (56), to be linear in creation and annihilation operators, which may simplify the analysis.

The Pauli-Fierz transformation (57) is very useful in the analysis of the original Hamiltonian (37) as well. Its effect is to replace $A(x)$ by $A(x) - A(0) = \phi(G_x - G_0)$ where

$$|G_x(k) - G_0(k)| = \left| \frac{\kappa(k)}{\sqrt{|k|}}(e^{ik \cdot x} - 1) \right| \leq |k|^{1/2} |\kappa(k)||x|.$$ 

Thus the IR-singularity of the form-factor in $UHU^*$ is reduced by one power of $|k|$ at the expense of the unbounded factor $|x|$. This factor, however, is compensated by the exponential decay whenever the total energy is below the ionization threshold (see Section 2.4).
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