One Electron Molecules with Relativistic Kinetic Energy: Properties of the Discrete Spectrum

Ingrid Daubechies*

Theoretische Natuurkunde, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium

Abstract. We discuss the discrete spectrum of the operator

$$H_K(c) = [-\hbar^2 c^2 \Delta + m^2 c^4]^{1/2} - \sum_{k=1}^{K} Z_k e^2 |x - R_k|^{-1}.$$

More specifically, we study 1) the behaviour of the eigenvalues when the internuclear distances contract, 2) the existence of a c-independent lower bound for $H_K(c) - mc^2$, 3) the nonrelativistic limit of the eigenvalues of $H_K(c) - mc^2$.

1. Introduction

This paper deals with the operator

$$H_K = (-\hbar^2 c^2 \Delta + m^2 c^4)^{1/2} - \sum_{k=1}^{K} Z_k e^2 |x - R_k|^{-1} \tag{1}$$

describing a relativistic charged particle with mass m in the presence of K fixed nuclei (Born-Oppenheimer approximation). The kinetic energy operator for the charged particle is obtained by straightforward "quantization" of the relativistic formula for the kinetic energy $[p^2 c^2 + m^2 c^4]^{1/2}$; (1) can be considered as an alternative to the Klein-Gordon equation for a relativistic model neglecting spin effects. In what follows we shall, with a slight abuse of terminology, use the name "electron" for the charged particle described by (1).

For the case $K = 1$ the above operator has been studied in detail by Herbst [1] and Weder [2]. One finds that

$$H_1 = (-\hbar^2 c^2 \Delta + m^2 c^4)^{1/2} - Z e^2 |x|^{-1}$$

is bounded below if and only if the nuclear charge Z is less than a critical value Z_{crit}. This phenomenon is typical for relativistic atom models; the value for Z_{crit} in the

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* "Wetenschappelijk medewerker" at the Interuniversitair Instituut voor Kernwetenschappen, Belgium

present case, $Z_{\mathrm{crit}} = 2\alpha^{-1}/\pi$ [where $\alpha = e^2/\hbar c \approx (137)^{-1}$], lies between the corresponding critical values for the Dirac and Klein-Gordon theories (where $Z_{\mathrm{crit}} = \alpha^{-1}$ and $\alpha^{-1}/2$, respectively). For $Z < Z_{\mathrm{crit}}$ the discrete spectrum of H_1 consists of infinitely many eigenvalues between 0 and mc^2, accumulating at mc^2; the remainder of the spectrum is purely absolutely continuous and consists of the half line $[mc^2, \infty)$. Moreover [1], the eigenvalues of H_1 are separated from 0 by a gap increasing with $Z - Z_{\mathrm{crit}}$:

$$\sigma_{\mathrm{disc}}(H_1) \subset [(1 - Z^2/Z_{\mathrm{crit}}^2)^{1/2} mc^2, mc^2). \tag{2}$$

In the nonrelativistic limit, this gives a lower bound on the difference between the ground state energy E_0 of H_1 and the rest energy mc^2:

$$E_0(H_1) - mc^2 \geqq -(\pi^2/8)Z^2 e^4 m \hbar^{-2} + O(c^{-2}). \tag{3}$$

Up to terms of order c^{-2} this lower bound is independent of c; it has the same dependence on Z, e, m, and $\hbar$ as the ground state of the true hydrogenic atom [the coefficient $\pi^2/8$ is larger than the true coefficient $1/2$, but after all, (3) only gives a lower bound].

For arbitrary values of K, a first study of H_K was made in [3]. As in the case $K = 1$, the operator H_K is bounded below if and only if $Z_k \leqq Z_{\mathrm{crit}} = 2\alpha^{-1}/\pi$, for all k. We shall always restrict ourselves to this case. Again one finds for $Z_k < Z_{\mathrm{crit}}$, that the essential spectrum of H_K is the half-line $[mc^2, \infty)$. If $\sum_{k=1}^{K} Z_k > Z_{\mathrm{crit}}$, negative eigenvalues occur [unlike the $K = 1$ case: see (2)], which may be made arbitrarily negative by bringing the nuclei close enough together. This "collapsing" tendency is, however, held in check by the electrostatic repulsion between the nuclei: it was proved in [3] that the total energy (including the electrostatic repulsion between the nuclei) for the ground state of the one electron – K nucleus – system is positive:

$$E_0(H_K) + \sum_{\substack{k,l=1 \\ k<l}}^{K} Z_k Z_l e^2 |R_k - R_l|^{-1} \geqq 0. \tag{4}$$

This means that the system is stable (see [3]).

In the present paper we want to address three further questions concerning the spectrum of H_K: 1) the behaviour of the energy levels when the internuclear distances $|R_k - R_l|$ tend to zero, 2) the existence of a lower bound analoguous to (2), for the case $K \neq 1$, and 3) the non-relativistic limit of the eigenvalues of H_K.

When the electron mass is put equal to zero, $m = 0$, it is easy to see what happens if the $|R_k - R_l|$ all shrink to zero. If $\sum_{k=1}^{K} Z_k > Z_{\mathrm{crit}}$, one finds that $h_K(\mathbf{R}) = H_K(m = 0; \mathbf{R})$ has non-empty discrete spectrum (we use the notation $\mathbf{R}$ for the set $\{R_k\}_{k=1,\ldots,K}$). Since $h_K(\mathbf{R})$ and $\lambda h_K(\lambda \mathbf{R})$ are unitarily equivalent, the eigenvalues $e_n(\mathbf{R})$ of h_K have the property

$$e_n(\lambda \mathbf{R}) = \lambda^{-1} e_n(\mathbf{R}). \tag{5}$$

As λ tends to zero, the eigenvalues of $h_K(\lambda \mathbf{R})$ all tend to $-\infty$. We prove in Sect. 2 that a similar phenomenon takes place if the electron mass is different from zero:

Theorem 1. *Let H_K be defined as in (1), with $0 \leqq Z_k \leqq Z_{crit}$ for all k. Suppose that $\sum_{k=1}^{K} Z_k > Z_{crit}$. Then $\forall E < 0$, $\forall N_0 \in \mathbb{N}$: $\exists \lambda_0$ such that*

$$\lambda \leqq \lambda_0 \quad \Rightarrow \quad \#\{E_n; E_n \text{ eigenvalue of } H_K(\lambda\mathbf{R}), E_n < E\} \geqq N_0.$$

A similar theorem for the Dirac operator with several Coulomb singularities, where E can be chosen arbitrarily in $]-mc^2, mc^2[$, was proved by Klaus [4]. Our proof of the above theorem is inspired by the proofs given in [4]: the essential ingredients are the use of the Birman-Schwinger-kernel, and an argument using strong resolvent convergence.

In Sect. 3 we prove a lower bound for H_K analogous to (2). The following simple argument already gives such a lower bound. For fixed $Z_1, ..., Z_K$, there exists a value c_0 of c such that $\sum_{k=1}^{K} Z_k \leqq (2/\pi)\hbar c_0/e^2$. The same argument used by Herbst in [1] to obtain (2) can then be applied in the present case, and we have $\left(Z_{tot} = \sum_k Z_k\right)$:

$$c \geqq c_0 \quad \Rightarrow \quad \sigma_{disc}(H_K) \subset [(1 - Z_{tot}^2/Z_{crit}^2)^{1/2}mc^2, mc^2) \tag{6}$$

[where again $Z_{crit} = (2/\pi)(e^2/\hbar c)^{-1}$]. This lower bound seems to be non-optimal from two points of view:

1) It is only valid for large enough values of c; the lower limit c_0 depends on the choice for the Z_k. It would be rather surprising if this were the best one can do.

2) If the nuclei are widely enough separated, one would expect the electron to settle around the nucleus with the largest charge without "seeing" the other nuclei. This would be reflected by a dependence of the lower bound on $Z_{max} = \max\{Z_k; k = 1, ..., K\}$ rather than on Z_{tot}. Both these criticisms of (6) are avoided by the following theorem, proved in Sect. 3:

Theorem 2. *For any K, and any $Z_1 ... Z_K$ with*

$$6 \leqq \max_k Z_k \leqq (2/\pi)\hbar c/e^2 = Z_{crit},$$

we have

$$H_K + \sum_{\substack{k,l=1 \\ k<l}}^{K} Z_k Z_l e^2 |R_k - R_l|^{-1} \geqq mc^2[1 - (\max Z_k)^2/Z_{crit}^2]^{1/2}. \tag{7}$$

For $\max_k Z_k < 6$ we prove a weaker result (see Sect. 3). The proof of (7) uses a lower bound similar to but stronger than (4), which was also proved in [3]. Note that (7) contains the electrostatic repulsion between the nuclei: if the nuclei are far apart, this term becomes negligible, and (7) is a much better bound than (6); if the nuclei are very close however, the repulsion energy becomes rather large, and (6) may be better than (7).

Finally, in Sect. 4, we study the nonrelativistic limit (i.e. $c \to \infty$) of the eigenvalues of $H_K(c)$. The lower bounds (6) and (7) already imply a nonrelativistic lower bound for the ground state energy $E_0(H_K) - mc^2$, similar to (3). As we noted

above, these nonrelativistic lower bounds for the ground state energy are too small by a factor $\pi^2/4$ when compared with the expected limit. Moreover, these lower bounds cannot give us any information concerning the excited states. We prove in Sect. 4 that *all* the energy levels of H_K tend to the corresponding bound state energy levels of the nonrelativistic Hamiltonian when $c \to \infty$:

Theorem 3. *Define*

$$H_K^0 = -(\hbar^2/2m)\Delta - \sum_{k=1}^{K} Z_k e^2 |x - R_k|^{-1}. \tag{8}$$

Let $E_n(c)$, E_n^0 respectively be the nth eigenvalues (counting multiplicity) of $H_K(c)$, H_K^0, where $H_K(c)$ is given by (1). Then $\lim\limits_{c \to \infty} [E_n(c) - mc^2] = E_n^0$.

To prove this, we show that there exists a c-independent z in $\mathbb{C}$ such that the resolvent $(H_K(c) - mc^2 - z)^{-1}$ is norm continuous in c^{-1} around the nonrelativistic limit $c^{-1} = 0$. The proof uses the fact that (7) implies the existence of a c-independent lower bound for $H_K(c) - mc^2$.

2. The Behaviour of the Eigenvalues under Contractions

For this and the next section we shall use units such that $\hbar = c = 1$. We can then rewrite H_K as

$$H_K = (p^2 + m^2)^{1/2} - V_{\mathbf{R}}(x),$$

where $p^2 = -\Delta$, and

$$V_{\mathbf{R}}(x) = \sum_{k=1}^{K} Z_k (e^2/\hbar c) |x - R_k|^{-1} = (2/\pi) \sum_{k=1}^{K} \mu_k |x - R_k|^{-1}, \tag{9}$$

with $\mu_k = Z_k/Z_{\text{crit}}$.

We consider the situation in which $M \equiv \sum\limits_{k=1}^{K} \mu_k > 1$; as always we have $\mu_k \leq 1$ for all k, hence $\mu \equiv \max\limits_{k} \mu_k \leq 1$.

According to the Birman-Schwinger principle, we have, for $E < 0$,

$$\# \{E_n ; E_n \text{ eigenvalue of } H_K, E_n < E\}$$
$$= \# \{e_n ; e_n \text{ eigenvalue of } V_{\mathbf{R}}^{1/2}[(p^2 + m^2)^{1/2} + |E|]^{-1} V_{\mathbf{R}}^{1/2}, e_n > 1\}.$$

We shall therefore make a study of the spectrum of

$$V_{\mathbf{R}}^{1/2}[(p^2 + m^2)^{1/2} + |E|]^{-1} V_{\mathbf{R}}^{1/2}.$$

We shall show that on the one hand

$$\sigma_{\text{ess}}(V_{\mathbf{R}}^{1/2}[(p^2 + m^2)^{1/2} + |E|]^{-1} V_{\mathbf{R}}^{1/2}) = [0, \mu], \tag{10}$$

while on the other hand every point in $[0, M]$ is an accumulation point of

$$\bigcup_{n} \sigma(V_{\mathbf{R}/n}^{1/2}[(p^2 + m^2)^{1/2} + |E|]^{-1} V_{\mathbf{R}/n}^{1/2})$$

(see below). Since $M > 1 \geqq \mu$, this will imply that the number of eigenvalues greater than 1 of the operator $V_{\mathbf{R}/n}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\mathbf{R}/n}^{1/2}$ tends to infinity for $n \to \infty$.

We first compute the spectrum of $|x|^{-1/2}|p|^{-1}|x|^{-1/2}$, where $|p| = (-\varDelta)^{1/2}$.

Lemma. $\sigma(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) = \sigma_{\mathrm{ac}}(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) = [0, \pi/2]$.

Proof. Since $|x|^{-1/2}|p|^{-1}|x|^{-1/2} \geqq 0$, and $\||p|^{-1/2}|x|^{-1/2}\| = (\pi/2)^{1/2}$ (see [1]), we obviously have $\sigma(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) \subset [0, \pi/2]$. We prove that this inclusion is an equality by explicit computation. On $L^2(\mathbb{R}^3)$, the operator $|x|^{-1/2}|p|^{-1}|x|^{-1/2}$ has integral kernel

$$(2\pi^2)^{-1}|x|^{-1/2}|x-y|^{-2}|y|^{-1/2}.$$

Defining the unitary operator U from $L^2(\mathbb{R}^3)$ to $L^2(\mathbb{R} \times S^2)$ by

$$(Uf)(t, \omega) = e^{3t/2}f(e^t\omega),$$

one finds that on $L^2(\mathbb{R} \times S^2)$ the operator

$$U|x|^{-1/2}|p|^{-1}|x|^{-1/2}U^{-1}$$

is given by the integral kernel

$$F(t_1, t_2; \omega_1, \omega_2) = (4\pi^2)^{-1}[\cosh(t_1-t_2)-\omega_1 \cdot \omega_2]^{-1}.$$

Since F depends only on the difference $t_1 - t_2$, we see that by a Fourier transform $|x|^{-1/2}|p|^{-1}|x|^{-1/2}$ is unitarily equivalent to the operator B on $L^2(\mathbb{R} \times S^2)$ defined by

$$(Bf)(k, \omega) = \int d\omega' b(k; \omega, \omega') f(k, \omega')$$

with

$$b(k; \omega, \omega') = \int dt e^{ikt} F(t, 0; \omega, \omega')$$

$$= (2\pi)^{-1}[1-(\omega \cdot \omega')^2]^{-1/2} \frac{\sinh[k(\pi-\cos^{-1}\omega \cdot \omega')]}{\sinh k\pi},$$

where we choose $\cos^{-1}\omega \cdot \omega' \in [0, \pi]$.

Since the integral kernel $b(k; \omega, \omega')$ depends only on $\omega \cdot \omega'$, B can be written as a direct sum $\bigoplus\limits_{l=0}^{\infty} \bigoplus\limits_{m=-l}^{l} B_{lm}$, where each B_{lm} acts on $L^2(\mathbb{R})$ and is given by an integral kernel too:

$$(B_{lm}f)(k) = b_{lm}(k)f(k),$$

with

$$b_{lm}(k) = \int\limits_{S^2} d\omega_1 \int\limits_{S^2} d\omega_2 \overline{Y_{lm}(\omega_1)} Y_{lm}(\omega_2) b(k; \omega_1, \omega_2).$$

One can check that each of these functions b_{lm} is continuous, tending to zero for $k \to \infty$. This implies that $|x|^{-1/2}|p|^{-1}|x|^{-1/2}$ has only absolutely continuous spectrum. Moreover one finds $b_{00}(0) = \pi/2$, hence $b_{00}(\mathbb{R}) = [0, \pi/2]$, which implies

$$\sigma(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) \supset \sigma(B_{00}) = b_{00}(\mathbb{R}) = [0, \pi/2]. \quad \square$$

In the following proposition we prove how this implies (10).

Proposition. *Let $V_{\mathbf{R}}$ be defined as in (9), with $R_k \neq R_l$ for $k \neq l$. Then*

$$\sigma_{\mathrm{ess}}(V_{\mathbf{R}}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\mathbf{R}}^{1/2}) = \sigma_{\mathrm{ess}}(V_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2})$$
$$= (2/\pi)\mu\,\sigma_{\mathrm{ess}}(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) = [0,\mu]\,.$$

Proof. For B_1, B_2 bounded operators, we shall use the notation $B_1 =_c B_2$ if $B_1 - B_2$ is compact. Choose a strictly positive δ such that $2\delta < |R_k - R_l|$ for all $k \neq l$. Define $f_k(x) = 1$ if $|x - R_k| \leq \delta$, $f_k(x) = 0$ otherwise. Define $f = \sum_k f_k$. Since $(|p|+1)^{-1/2}V_{\mathbf{R}}^{1/2}$ is bounded, we have (n-lim = norm limit)

$$(|p|+1)^{-1}V_{\mathbf{R}}^{1/2} = n\text{-}\lim_{\varepsilon \to 0} e^{-\varepsilon p^2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}\,.$$

Moreover

$$e^{-\varepsilon p^2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2} = n\text{-}\lim_{\lambda \to 0} e^{-\varepsilon p^2}(|p|+1)^{-1}[f(x)V_{\mathbf{R}}^{1/2} + V_{\mathbf{R}}^{1/2}(1-f(x))e^{-\lambda x^2}]$$

is a compact operator (as the norm limit of Hilbert-Schmidt operators), which implies that $(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}$ is compact. Since

$$|E| - 1 \leq (p^2+m^2)^{1/2} + |E| - (|p|+1) \leq |E| + m - 1\,,$$

we have therefore

$$V_{\mathbf{R}}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\mathbf{R}}^{1/2} =_c V_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}\,;$$

this proves the first equality of the proposition (by Weyl's theorem). Since $(1-f)V_{\mathbf{R}}^{1/2}$ is bounded, we have also

$$V_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2} =_c fV_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}f\,. \tag{11}$$

It is easy to check that $fV_{\mathbf{R}}^{1/2} - \sum_k f_k(x)(2\mu_k/\pi)^{1/2}|x-R_k|^{-1/2}$ is bounded. Using the fact that $|p|-1$ has integral kernel $(2\pi^2)^{-1}|x-y|^{-2}$, one sees moreover that

$$f_k|x-R_k|^{-1/2}(|p|+1)^{-1}|x-R_l|^{-1/2}f_l$$

is Hilbert-Schmidt for $k \neq l$. Hence

$$fV_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}f =_c (2/\pi)\sum_k \mu_k f_k|x-R_k|^{-1/2}(|p|+1)^{-1}|x-R_k|^{-1/2}f_k\,. \tag{12}$$

Since the f_k are the characteristic functions of disjoint balls, the sum in the right hand member of (12) can be considered as a direct sum of unitarily equivalent operators (up to the coefficients μ_k). Defining $g(x) = 1$ if $|x| \leq \delta$, $g(x) = 0$ otherwise, we can therefore conclude from (11) and (12) that $\sigma_{\mathrm{ess}}(V_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2})$ is completely determined by

$$\sigma(g|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}g)\,.$$

Again, we have that $(1-g)|x|^{-1/2}$ is bounded, while $(|p|+1)^{-1}|x|^{-1/2}$ is compact, which implies

$$g|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}g =_c |x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}\,.$$

Hence

$$\sigma_{\text{ess}}(g|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}g) = \sigma_{\text{ess}}(|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}). \qquad (13)$$

One easily sees that all the operators $|x|^{-1/2}(|p|+\lambda)^{-1}|x|^{-1/2}$, $\lambda > 0$, are unitarily equivalent under dilations. This implies that $\sigma(|x|^{-1/2}(|p|+\lambda)^{-1}|x|^{-1/2})$ is independent of λ. On the other hand $|x|^{-1/2}(|p|+\lambda)^{-1}|x|^{-1/2}$ converges strongly to $|x|^{-1/2}|p|^{-1}|x|^{-1/2}$ for $\lambda \to 0$. This implies that every $e \in \sigma(|x|^{-1/2}|p|^{-1}|x|^{-1/2})$ can be written as $e = \lim_{n \to \infty} e_n$, with

$$e_n \in \sigma(|x|^{-1/2}(|p|+1/n)^{-1}|x|^{-1/2}).$$

Combining these two facts gives

$$[0, \pi/2] = \sigma(|x|^{-1/2}|p|^{-1}|x|^{-1/2}) \subset \sigma(|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}).$$

Since also

$$0 \leq |x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2} \leq |x|^{-1/2}|p|^{-1}|x|^{-1/2} \leq \pi/2,$$

we find $\sigma(|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}) = [0, \pi/2]$, hence, by (13), and because

$$0 \leq g|x|^{-1/2}(|p|+1)^{-1/2}|x|^{-1/2}g \leq \pi/2,$$

$$\sigma(g|x|^{-1/2}(|p|+1)^{-1}|x|^{-1/2}g) = [0, \pi/2].$$

Together with (11) and (12) this implies $\left(\mu = \max_k \mu_k\right)$

$$\sigma_{\text{ess}}(V_{\mathbf{R}}^{1/2}(|p|+1)^{-1}V_{\mathbf{R}}^{1/2}) = [0, \mu]. \qquad \square$$

With the help of this proposition we can now prove Theorem 1.

Proof of Theorem 1. We have (s-lim = strong limit)

$$s\text{-}\lim_{\lambda \to 0} V_{\lambda\mathbf{R}}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\lambda\mathbf{R}}^{1/2}$$

$$= (2M/\pi)|x|^{-1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}|x|^{-1/2} \qquad (14)$$

$\Big[$all these operators are bounded, and $V_{\lambda\mathbf{R}} \xrightarrow[\lambda \to 0]{} (2M/\pi)|x|^{-1}$ a.e., where

$M = \sum_k \mu_k \Big]$.

For $\lambda \to 0$, we have

$$\sigma_{\text{ess}}(V_{\lambda\mathbf{R}}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\lambda\mathbf{R}}^{1/2}) = [0, \mu],$$

while

$$\sigma_{\text{ess}}((2M/\pi)|x|^{-1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}|x|^{-1/2}) = [0, M].$$

Since $\mu \leq 1 < M$, the strong convergence (14) implies that every $e \in (1, M]$ can be written as $e = \lim_{n \to \infty} e_n$, with e_n an *eigenvalue* larger than 1 of

$$V_{\mathbf{R}/n}^{1/2}[(p^2+m^2)^{1/2}+|E|]^{-1}V_{\mathbf{R}/n}^{1/2}$$

(see Theorem VIII.24 in [5]). One easily sees that this implies

$$\lim_{n \to \infty} \# \{e > 1; e \text{ eigenvalue of } V_{\mathbf{R}/n}^{1/2}[(p^2 + m^2)^{1/2} + |E|]^{-1} V_{\mathbf{R}/n}^{1/2}\} = \infty.$$

By the Birman-Schwinger principle this implies $(E < 0)$

$$\lim_{n \to \infty} \# \{e < E; e \text{ eigenvalue of } (p^2 + m^2)^{1/2} - V_{\mathbf{R}/n}\} = \infty. \tag{15}$$

Since $(p^2 + m^2)^{1/2} - V_{\lambda \mathbf{R}}$ is unitarily equivalent with

$$\lambda^{-1}[(p^2 + \lambda^2 m^2)^{1/2} - V_{\mathbf{R}}],$$

the negative eigenvalues of $(p^2 + m^2)^{1/2} - V_{\lambda \mathbf{R}}$ decrease monotonically as $\lambda \searrow 0$. Together with (15) this proves the theorem. $\square$

Remarks. 1. Using the continuity in λ of the eigenvalues of $(p^2 + m^2)^{1/2} - V_{\lambda \mathbf{R}}$ (which follows from the unitary equivalence of this operator with $\lambda^{-1}[(p^2 + \lambda^2 m^2)^{1/2} - V_{\mathbf{R}}])$, one can rewrite the conclusion of Theorem 1 as:

$$\forall E < 0, \quad \forall \lambda_0 : \# \{\lambda < \lambda_0; E \in \sigma((p^2 + m^2)^{1/2} - V_{\lambda \mathbf{R}})\} = \infty.$$

It is in this form that the analogous theorem for Dirac operators was stated in [4].

2. In order for the conclusion of Theorem 1 to hold, it is not really necessary that all the internuclear distances shrink to zero, nor that the shrinking is an orderly, simultaneous contraction. The argument of the proof also works in the following situation. Let S be any subset of $\{1, \dots, K\}$ such that $\sum_{k \in S} \mu_k > 1$. Define

$$d_S = \max \{|R_k - R_l|; k, l \in S\}.$$

Then, for any $E < 0$,

$$\# \{e < E; e \text{ eigenvalue of } (p^2 + m^2)^{1/2} - V_{\mathbf{R}}\}$$

tends to ∞ as d_S tends to zero.

3. If we put $m = 0$, we find that $|p| - V_{\lambda \mathbf{R}}$ and $\lambda^{-1}(|p| - V_{\mathbf{R}})$ are unitarily equivalent. The number of negative eigenvalues of $|p| - V_{\lambda \mathbf{R}}$ is therefore independent of λ, which implies that $|p| - V_{\mathbf{R}}$ has infinitely many negative eigenvalues if $\sum_{k=1}^{K} \mu_k > 1$.

3. A Lower Bound on H_K

Following the same strategy as in [3], we shall first prove (7) in the case where all the Z_k are equal, and then use a concavity argument to extend this result to arbitrary Z_k.

Proposition. *Take* $6 \le Z \le Z_{\text{crit}} = (2/\pi)\alpha^{-1}$. *Then*

$$(p^2 + m^2)^{1/2} - Z\alpha \sum_{k=1}^{K} |x - R_k|^{-1} + Z^2 \alpha \sum_{\substack{k, l = 1 \\ k < l}}^{K} |R_k - R_l|^{-1} \ge m[1 - Z^2/Z_{\text{crit}}^2]^{1/2}. \tag{16}$$

Proof. The following inequality [stronger than (4)] was proved in [3]:

$$|p| - (2/\pi) \left[\sum_{k=1}^{K} |x - R_k|^{-1} - 6 \sum_{\substack{k,l=1 \\ k<l}}^{K} |R_k - R_l|^{-1} \right] \geqq 0 .$$

This implies

$$|p|^{-1/2} \left(Z\alpha \sum_{k=1}^{K} |x - R_k|^{-1} - 6Z\alpha \sum_{\substack{k,l=1 \\ k<l}}^{K} |R_k - R_l|^{-1} \right) |p|^{-1/2} \leqq Z/Z_{\text{crit}} .$$

With the notation

$$v(x) = Z\alpha \sum_{k=1}^{K} |x - R_k|^{-1} - Z^2\alpha \sum_{\substack{k,l=1 \\ k<l}}^{K} |R_k - R_l|^{-1} ,$$

we have therefore

$$Z \geqq 6 \Rightarrow |p|^{-1/2} v |p|^{-1/2} \leqq Z/Z_{\text{crit}} .$$

For $Z = Z_{\text{crit}}$, (16) was already proved in [3]. We shall therefore assume $Z < Z_{\text{crit}}$.

We now borrow an argument from [1] to prove (16). Fix $\lambda \in [0, m)$, and define $H_0 = (p^2 + m^2)^{1/2}$. Then

$$B \equiv (H_0 - \lambda)^{-1/2} v (H_0 - \lambda)^{-1/2} \leqq (Z/Z_{\text{crit}}) \| (H_0 - \lambda)^{-1/2} |p|^{1/2} \|^2$$

$$= (Z/Z_{\text{crit}}) m (m^2 - \lambda^2)^{-1/2} .$$

This implies that $\mathbb{1} - B$ is invertible for $\lambda < m[1 - Z^2/Z_{\text{crit}}^2]^{1/2}$, hence that

$$(H_0 - v - \lambda)^{-1} = (H_0 - \lambda)^{-1/2} (\mathbb{1} - B)^{-1} (H_0 - \lambda)^{-1/2}$$

is a bounded operator. We have therefore proved that

$$[0, m(1 - Z^2/Z_{\text{crit}}^2)^{1/2}) \subset \varrho(H_0 - v) .$$

Since $H_0 - v \geqq 0$ by (4), this proves (16). □

By means of a concavity argument we can extend this to obtain the following result:

Proposition. *Fix* $\tilde{Z}$, *with* $6 \leqq \tilde{Z} \leqq Z_{\text{crit}}$. *Choose* $Z_1, ..., Z_K$ *such that* $0 \leqq Z_k \leqq \tilde{Z}$ *for all* k. *Then*

$$(p^2 + m^2)^{1/2} - \sum_{k=1}^{K} Z_k \alpha |x - R_k|^{-1} + \sum_{k<l} Z_k Z_l \alpha |R_k - R_l|^{-1} \geqq m(1 - \tilde{Z}^2/Z_{\text{crit}}^2)^{1/2} .$$

$$\tag{17}$$

Proof. We use the notation $\mathbf{Z}$ for the set $\{Z_1, ..., Z_K\}$. Define for all $\mathbf{Z} \in [0, \tilde{Z}]^K$,

$$G(\mathbf{Z}) = \inf \operatorname{spec} \left\{ (p^2 + m^2)^{1/2} - \sum_{k=1}^{K} Z_k \alpha |x - R_k|^{-1} - m(1 - \tilde{Z}^2/Z_{\text{crit}}^2)^{1/2} \right\} .$$

$G(\mathbf{Z})$ is a jointly concave function in the Z_k. According to (16) we have at every cornerpoint $\mathbf{P}$ of the cube $[0, \tilde{Z}]^K$,

$$G(\mathbf{P}) \geqq - \sum_{k<l} P_k P_l \alpha |R_k - R_l|^{-1} .$$

By concavity it follows that (see Lemma 2.3 in [3])

$$G(\mathbf{Z}) \geqq - \sum_{k<l} Z_k Z_l \alpha |R_k - R_l|^{-1} \quad \text{for all} \quad \mathbf{Z} \in [0, \tilde{Z}]^K. \quad \square$$

Theorem 2, as it was stated in the introduction, is essentially a reformulation of this last proposition: for given $Z_1, ..., Z_K$, with $Z_{\max} = \max_k Z_k \geqq 6$, we choose $\tilde{Z} = Z_{\max}$; the theorem then follows immediately.

If $Z_{\max} < 6$, one can always choose $\tilde{Z} = 6$, which gives for $Z_1, ..., Z_K < 6$:

$$(p^2 + m^2)^{1/2} - \sum_{k=1}^{K} Z_k \alpha |x - R_k|^{-1} + \sum_{k<l} Z_k Z_l \alpha |R_k - R_l|^{-1} \geqq m(1 - 36/Z_{\text{crit}}^2)^{1/2}. \tag{18}$$

If all the Z_k are chosen equal, $Z_k = Z$, and the limit $Z \to 0$ is taken, one expects that the ground state $E_0(H_K)$ approaches m: $\lim_{Z \to 0} E_0(H_K) = m$, physically. This is not reflected by the lower bound (18). Actually, we can do slightly better than (18). If we define $G(\mathbf{Z})$ as above, we obviously have

$$G(\mathbf{O}) \geqq m(1-a), \qquad G(\mathbf{Q}_j) \geqq 0, \quad \text{where} \quad a = (1 - 36/Z_{\text{crit}}^2)^{1/2}$$

(we assume $Z_k \leqq 6$, for all k), and where $\mathbf{O}, \mathbf{Q}_j$ are K-tuples defined as $\mathbf{O} = (0, ..., 0)$ (all entries zero), $\mathbf{Q}_j = (0, ..., 0, 6, 0, ..., 0)$ (all entries zero except the jth which equals 6). By concavity this implies ($Z_k \leqq 6$)

$$G(\mathbf{Z}) \geqq m(1-a)\left(1 - \sum_k Z_k/6\right) \quad \text{if} \quad \sum_k Z_k \leqq 6,$$

hence

$$G(\mathbf{Z}) \geqq - \sum_{k<l} Z_k Z_l \alpha |R_k - R_l|^{-1} + m(1-a) \max\left(1 - \sum_k Z_k/6, 0\right).$$

For $Z_1, ..., Z_K < 6$, this can be rewritten as:

$$(p^2 + m^2)^{1/2} - \sum_{k=1}^{K} Z_k \alpha |x - R_k|^{-1} + \sum_{k<l} Z_k Z_l \alpha |R_k - R_l|^{-1}$$

$$\geqq m\left\{1 - \min\left(1, \sum_k Z_k/6\right)[1 - (1 - 36/Z_{\text{crit}}^2)^{1/2}]\right\}. \tag{19}$$

This lower bound has the advantage of tending to m when all the Z_k are equal and tend to zero. However, we strongly suspect that (19) is not optimal; physically one would believe that Theorem 2 holds without restriction on $\max Z_k$.

Remark. Note that (17) implies the existence of a c-independent lower bound for $H_K(c) - mc^2$. Re-introducing c, we see from (17) that

$$(p^2 c^2 + m^2 c^4)^{1/2} - mc^2 - \sum_{k=1}^{K} Z_k e^2 |x - R_k|^{-1}$$

$$\geqq - \sum_{k<l} Z_k Z_l e^2 |R_k - R_l|^{-1} + mc^2[(1 - a^2 c^{-2})^{1/2} - 1], \tag{20}$$

with $a = c \max(6, \{Z_k\})/Z_{\text{crit}} = (e^2 \pi/2\hbar) \max(6, \{Z_k\})$. Expression (20) implies

$$H_K(c) - mc^2 \geqq - \sum_{k<l} Z_k Z_l e^2 |R_k - R_l|^{-1} - ma^2 \equiv -b(\mathbf{Z}, \mathbf{R}). \tag{21}$$

4. The Nonrelativistic Limit

The naive way of obtaining the nonrelativistic limit of $H_K(c) - mc^2$ would be to write

$$(p^2 c^2 + m^2 c^4)^{1/2} - mc^2 = p^2/2m + O(c^{-2}), \tag{22}$$

and to apply perturbation theory. This is actually what the Foldy-Wouthuysen approach [5] does for the more complicated Dirac case. One readily sees however that the next term in the development (22) is $- -(p^4/8m^3)c^{-2}$, which is far too singular to be considered as a "perturbation" of the zeroth order term $p^2/2m$. The same problem occurs in the Foldy-Wouthuysen derivation of the nonrelativistic limit of the Dirac Hamiltonian. Recently Gesztesy, Grosse, and Thaller showed that the proper way of looking at the nonrelativistic limit of a Dirac Hamiltonian is to study the resolvent. They showed that the Dirac resolvent is holomorphic in c^{-1} around its nonrelativistic limit $c^{-1} = 0$ [7], and obtained powerful results concerning the analyticity of the eigenvalues in c^{-2}, and an explicit formula, for the first order relativistic correction term to the nonrelativistic eigenvalues [8] (simpler than Foldy-Wouthuysen!). The same clue (i.e. studying the resolvent instead of the Hamiltonian itself) works in our present case. We have

Proposition. *Let $H_K(c)$, H_K^0 be defined as in (1), (8) respectively. Then for all $\mathbf{Z}, \mathbf{R}$, one can find $z \in \mathbb{C}$, c_0, and $k \geq 0$ such that $c \geq c_0 \Rightarrow z$ is in the resolvent sets of $H_K(c) - mc^2$ and H_K^0, and*

$$\|(H_K^0 - z)^{-1} - (H_K(c) - mc^2 - z)^{-1}\| \leq kc^{-1}. \tag{23}$$

Proof. Define $T^0 = p^2/2m$, $T(c) = (p^2 c^2 + m^2 c^4)^{1/2} - mc^2$, $V_{\mathbf{Z}}(x) = \sum_k Z_k e^2 |x - R_k|^{-1}$. Obviously $V_{\lambda \mathbf{Z}} = \lambda V_{\mathbf{Z}}$. Fix $\mathbf{Z}, \mathbf{R}$. Choose $\lambda > 1$, and define $c_0 = (\pi e^2/2\hbar)\lambda \max_k Z_k$. We have, using (21),

$$c \geq c_0 \Rightarrow T(c) - \lambda V_{\mathbf{Z}} = T(c) - V_{\lambda \mathbf{Z}} \geq -b(\lambda \mathbf{Z}, \mathbf{R}).$$

[The value of c_0 was chosen so as to ensure that $V_{\lambda \mathbf{Z}}$ is still $T(c)$-formbounded.] Put $b = \lambda^{-1} b(\lambda \mathbf{Z}, \mathbf{R})$. Then

$$(T(c) + \mathbb{1})^{-1/2}(V_{\mathbf{Z}} - b)(T(c) + \mathbb{1})^{-1/2} \leq \lambda^{-1}.$$

This implies that

$$\mathbb{1} - (T(c) + \mathbb{1})^{-1/2}(V - b)(T(c) + \mathbb{1})^{-1/2} \text{ is invertible } (V = V_{\mathbf{Z}}),$$

with $\|[\mathbb{1} - (T(c) + \mathbb{1})^{-1/2}(V - b)(T(c) + \mathbb{1})^{-1/2}]^{-1}\| \leq \lambda/(\lambda - 1)$.
    Choose $\beta \in \mathbb{R}$ large enough so that

$$\|(V - b)(T^0 + \mathbb{1} + i\beta)^{-1}\| \leq \lambda^{-1},$$

hence

$$\|[\mathbb{1} - (V - b)(T^0 + \mathbb{1} + i\beta)^{-1}]^{-1}\| \leq \lambda/(\lambda - 1).$$

Put now $z = -(b+1+i\beta)$. Then

$$[H_K(c) - mc^2 - z]^{-1} - [H_K^0 - z]^{-1}$$
$$= [H_K(c) - mc^2 - z]^{-1}[T^0 - T(c)][H_K^0 - z]^{-1}$$
$$= [T(c) - V + b + 1 + i\beta]^{-1}[T(c) - V + 1 + b][T(c) + \mathbb{1}]^{-1/2}$$
$$\cdot [\mathbb{1} - (T(c) + \mathbb{1})^{-1/2}(V - b)(T(c) + \mathbb{1})^{-1/2}]^{-1}$$
$$\cdot (T(c) + \mathbb{1})^{-1/2}[T^0 - T(c)](T^0 + \mathbb{1})^{-1}(T^0 + \mathbb{1})(T^0 + \mathbb{1} + i\beta)^{-1}$$
$$\cdot [\mathbb{1} - (V - b)(T^0 + \mathbb{1} + i\beta)^{-1}]^{-1}.$$

Hence

$$\|[H_K(c) - mc^2 - z]^{-1} - [H_K^0 - z]^{-1}\|$$
$$\leq \lambda^2/(\lambda - 1)^2 \|(T(c) + \mathbb{1})^{-1/2}[T^0 - T(c)](T^0 + \mathbb{1})^{-1}\|.$$

We have

$$\|(T(c) + \mathbb{1})^{-1/2}[T^0 - T(c)](T^0 + \mathbb{1})^{-1}\|$$
$$= \sup_{p \in \mathbb{R}^3} \{[(p^2c^2 + m^2c^4)^{1/2} - mc^2 + 1]^{-1/2}$$
$$\cdot [p^2/2m - (p^2c^2 + m^2c^4)^{1/2} + mc^2][1 + p^2/2m]^{-1}\}$$
$$= \sup_{t \in \mathbb{R}_+} \{(1 + t)^{-1/2}(t^2/2mc^2)(1 + t + t^2/2mc^2)^{-1}\}$$
$$\leq \sup_{t \in \mathbb{R}_+} \{(t^{1/2}/2mc^2)(1 + t/2mc^2)^{-1}\} \leq (8mc^2)^{-1/2}.$$

This proves (23), with $k = (8m)^{-1/2}\lambda^2/(\lambda - 1)^2$. $\square$

As a consequence of (23), the eigenvalues of $(H_K(c) - mc^2 - z)^{-1}$ tend to the eigenvalues of $(H_K^0 - z)^{-1}$ for $c \to \infty$, with a difference of order c^{-1} (or less). Since the eigenvalues of H correspond to the eigenvalues of the resolvent $(H - z)^{-1}$, this implies that the eigenvalues $E_n(c) - mc^2$ of $H_K(c) - mc^2$ tend to the eigenvalues E_n^0 of H_K^0, with again $|E_n(c) - mc^2 - E_n^0| \leq k_n c^{-1}$. This proves Theorem 3, formulated in the introduction.

Remark. It is clear that our estimate (21) is weak when compared with the results for the Dirac operator in [7, 8]. We have little doubt that stronger results also exist for our present operator $H_K(c)$. It seems improbable that the resolvent of $H_K(c) - mc^2$ would still be holomorphic in c^{-1}, because of the presence of the square root, but it is possible that the eigenvalues still are holomorphic. We have nothing to say about this.

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