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# On the Asymptotic Behaviour of Atomic Spectra near the Continuum

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Abstract. If  $\Sigma$  is the beginning of the continuous energy spectrum of an atom in any multiplet system, it is shown that this system contains groups of eigenvalues close to  $E_n = \Sigma - n^{-2}$ , compared with  $E_{n+1} - E_n$ , as  $n = 1, 2, \ldots \to \infty$ .

#### 1. Introduction

We consider the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i < k} \frac{e_i e_k}{|x_i - x_k|}$$

of a system of N charged particles, with centre of mass (CM) removed. The following is known about the spectrum  $\sigma(H)$  of H in any subspace of total angular momentum L or of given symmetry under permutations of identical particles:

- a)  $\sigma(H)$  consists of a continuum  $[\Sigma, \infty]$  and, in the complement of this continuum, only of eigenvalues with finite multiplicities which can accumulate only at  $\Sigma$ .  $\Sigma$  is the lowest threshold for break-up of the system into independent parts [1, 2].
- b) If  $\Sigma$  is the threshold for break-up into two sub-systems  $C_1$ ,  $C_2$  with total charges  $q_1$ ,  $q_2$  such that  $q_1q_2 < 0$ , then the number of eigenvalues below  $\Sigma$  is infinite. This is always the case for atoms [2].

Following a suggestion of SIMON [2], we want to study the asymptotic behaviour of the eigenvalues in case b). We introduce coordinates adapted to the decomposition  $(C_1, C_2)$  of the set of particles (1 ... N):

 $x \in R^3$  = position of the CM of  $C_2$  with respect to the CM of  $C_1$ ,  $y_i \in R^{(3n_i-3)}$  = internal coordinates for the system  $C_i$ , which are taken as linear combinations of the cartesian coordinates  $x_1 \ldots x_N$ .  $n_i$  stands for the number of particles in  $C_i$ .

If  $C_i$  has total mass  $M_i$ , we choose units such that  $\hbar = 1$ ,  $q_1q_2 = -2$ ,  $M_1^{-1} + M_2^{-1} = 2$ . Then H takes the form

$$H = p^2 + V(x, y_1, y_2) + h_1 + h_2,$$

where p = momentum conjugate to x, V = sum of all interactions linking  $C_1$  and  $C_2$ and  $h_i$  = Hamiltonian of  $C_i$  with CM removed. Now let

$$h_i \varphi_i = \varepsilon_i \varphi_i$$

for the ground state  $\varphi_i$  of  $C_i$ . For simplicity, we ignore possible degeneracies, and if  $C_i$ is a single particle we have, of course,  $h_i = 0$ ,  $\varepsilon_i = 0$ ,  $\varphi_i = 1$ . The operator

$$p^2 - 2|x|^{-1} + h_1 + h_2$$

has eigenvalues

$$E_n = \varepsilon_1 + \varepsilon_2 - n^{-2} = \Sigma - n^{-2}, \quad n = 1, 2...$$

of multiplicity  $n^2$  with eigenfunctions

$$\psi_n = \eta_n(x) \, \varphi_1(y_1) \, \varphi_2(y_2),$$

where  $\eta_n$  satisfies

$$(p^2-2|x|^{-1})\eta_n=-n^{-2}\eta_n.$$

We shall assume that  $\eta_n$ ,  $\varphi_1$ ,  $\varphi_2$ , are normalized to 1 in their respective  $L^2$ -spaces. Since  $V(x, y_1, y_2) \sim -2|x|^{-1}$  for bounded  $y_i$  and  $|x| \to \infty$  one expects  $E_n$ ,  $\psi_n$  to become 'approximate' eigenvalues and eigenfunctions of H as  $n \to \infty$ . More precisely, the question is how rapidly  $\|(H-E_n)\psi_n\| \to 0$  as  $n \to \infty$ . This question can be answered now that pointwise exponential bounds are available for the bound state wave functions  $\varphi_i$  [3].

# 2. Basic Inequalities

For real E and a > 0 let

$$N_a$$
 = spectral subspace of  $H$  where  $(H - E)^2 \le a^2$ . (1)

Suppose that M is a subspace of D(H) such that for all  $\psi \in M$ ,  $||\psi|| = 1$ ,

$$||(H-E)\psi|| \leqslant \varepsilon. \tag{2}$$

If  $\psi'$  is the component of  $\psi$  orthogonal to  $N_a$  we then have  $\varepsilon \ge ||(H-E)\psi'|| > a ||\psi'||$ , hence

$$\|\psi'\| = \operatorname{dist}(\psi, N_a) < \varepsilon a^{-1}. \tag{3}$$

Setting  $a = \varepsilon$  it follows that the projection of M onto  $N_{\varepsilon}$  is injective, hence

$$\dim N_{\varepsilon} \geqslant \dim M. \tag{4}$$

If  $E + \varepsilon < \Sigma$ , we conclude that H possesses eigenvalues of total multiplicity  $\geq \dim M$  in the interval  $[E - \varepsilon, E + \varepsilon]$ .

In order to deal with symmetries in the case of identical particles, we consider a projection P (projecting onto a subspace of given symmetry under permutations) commuting with H. Let M be as before and assume in addition to (2) that

$$||P\psi|| \geqslant \lambda$$
 (5)

for some  $\lambda > 0$  and all  $\psi \in M$ ,  $||\psi|| = 1$ . Then  $\dim PM = \dim M$  and

$$||(H-E)P\psi|| \leq \varepsilon \leq \varepsilon \lambda^{-1}||P\psi||.$$

Therefore, if  $E + \varepsilon \lambda^{-1} < \Sigma$ , HP possesses eigenvalues of total multiplicity  $\geqslant \dim M$  within the bounds  $E \pm \varepsilon \lambda^{-1}$  and  $\|P\psi\|^{-1}P\psi$  has distance less than  $\varepsilon(a\lambda)^{-1}$  from  $PN_a$ .

# 3. Estimate of $\|(H-E_n)\psi_n\|$

$$||(H - E_n)\psi_n|| = ||(V + 2|x|^{-1})\psi_n||$$

$$\leq \sum_{\substack{i \in C_1 \\ k \in C_2}} |e_i e_k| ||U_{ik}\psi_n||$$

with

$$\begin{split} U_{ik} &= |\; |x-z_1+z_2|^{-1} - |x|^{-1}| \\ &\leq |x|^{-1}|z_1-z_2|\; |x-z_1+z_2|^{-1}, \end{split}$$

where  $z_1(y_1)$ ,  $z_2(y_2)$  are the positions of particles i, k relative to the CM of  $C_1$ ,  $C_2$ , respectively. Therefore

$$||U_{ik}\psi_n||^2 \leqslant \int dx |x|^{-2} f(x) |\eta_n(x)|^2$$

with

$$f(x) = \int dz_1 dz_2 \, \rho_1(z_1) \, \rho_2(z_2) |z_1 - z_2|^2 |x - z_1 + z_2|^{-2},$$

where  $\rho_i$  is the probability density for  $z_i$  in the state  $\varphi_i$ . From the exponential bounds [3] for  $\varphi_i(y_i)$  it follows that  $\varphi_i(z) \leq \text{const} \cdot \exp(-\alpha |z|)$  for some  $\alpha > 0$ . Therefore,  $f(x) \leq \operatorname{const} |x|^{-2}$  and

$$||(H - E_n)\psi_n|| \le \operatorname{const}(\eta_n, |x|^{-4}\eta_n)^{1/2},$$
 (6)

with a constant independent of n and  $\eta_n$ . The matrix elements of  $|x|^{-4}$  in the conventional basis  $\eta_{nlm}(x) = R_{nl}(|x|) Y_{lm}(x/|x|) (l = 0, 1, ..., n-1; m = l, ..., -l)$  are known [4]:

$$(\eta_{nlm}, |x|^{-4}\eta_{nl'm'}) = \delta_{ll'}\delta_{mm'}[2n^5(l-\frac{1}{2})l(l+\frac{1}{2})(l+1)(l+\frac{3}{2})]^{-1}[3n^2 - l(l+1)]$$
 (7)

for l > 0. We now restrict  $\eta_n$  to the subspace spanned by the basis vectors  $\eta_{nlm}$  with

$$l+1 \geqslant n^{(2\alpha-3)/5} \quad (\alpha \leqslant 4) \tag{8}$$

the corresponding  $\psi_n$  then span a subspace  $M_n$  with

$$\dim M_n = n^2 - ([n^{(2\alpha-3)/5}] - 1)^2$$

where  $[a] = \text{smallest integer} \ge a$ . It follows from (6), (7) and (8) that for  $\alpha \le 4$ 

$$||(H - E_n)\psi_n|| \leqslant Cn^{-\alpha} \tag{9}$$

for all  $\psi_n \in M_n$ ,  $||\psi_n|| = 1$ , with C not depending on n,  $\psi_n$  or  $\alpha$ . From the inequalities of Section 2 we therefore obtain:

Theorem: There exists a constant C such that for  $3 < \alpha \le 4$  H possesses at least

$$n^2 - ([n^{(2\alpha-3)/5}] - 1)^2$$

eigenvalues (including multiplicities) in the intervals

$$I_n = [E_n - Cn^{-\alpha}, E_n + Cn^{-\alpha}],$$

if n is sufficiently large so that  $n^{-2} > Cn^{-\alpha}$ . For  $a_n = Cn^{-\beta}$ ,  $3 < \beta < \alpha$ , and all  $\psi_n \in M_n$ ,  $||\psi_n|| = 1$ ,

$$\operatorname{dist}(\psi_n, N_{a_n}) < n^{-(\alpha - \beta)},$$

where  $N_a$  and  $M_n$  are defined by (1) and (8).

Remarks: The conditions  $3 < \beta < \alpha$  merely serve to make the results significant. For example, the condition  $3 < \alpha$  implies that  $I_{n+1}$  is disjoint from  $I_n$  for n sufficiently large.

Is it necessary to increase l with n? For  $|x| \le n^2$  the radial Coulomb wave functions  $R_{nl}(|x|)$  behave like  $n^{-3/2}f_l(|x|)$  with  $f_l$  independent of n [5]. Therefore

$$||(H-E_n)\psi_n|| = O(n^{-3/2})$$

for fixed l and  $n \to \infty$ , and this decrease is too slow since  $\Sigma - E_n = n^{-2}$ . But even the first-order perturbation  $(\psi_n, (V+2|x|^{-1})\psi_n)$  of  $E_n$  is of the same order as  $E_{n+1} - E_n$ , namely  $O(n^{-3})$ . This shows the difficulty of proving a similar theorem in a subspace of fixed orbital angular momentum L.

Inclusion of short-range forces: The estimate (6) remains valid if V also contains two-body potentials  $W_{ik}(x_i - x_k)$  which are locally  $L^2$  and vanish at least like  $|x_i - x_k|^{-2}$  for  $|x_i - x_k| \to \infty$ .

### 4. Identical Particles

If the system contains identical particles, the theorem remains true in any sector of given symmetry, with C replaced by  $C\lambda^{-1}$ , provided that (5) holds with  $\lambda$  independent of n for n sufficiently large.

To prove (5) one only has to show that the overlap-integrals vanish as  $n \to \infty$ , i.e. that

$$\lim_{n\to\infty} \sup_{\substack{\psi_n\in M_n\\ \|\psi_n\|=1}} (\psi_n, \pi\psi_n) = 0, \tag{10}$$

where  $\pi\psi_n$  is obtained from  $\psi_n$  by a permutation  $\pi$  of identical particles which sends the partition  $(C_1, C_2)$  of  $(1 \dots N)$  into a different partition  $(C_1, C_2)$ . For a discussion of symmetries under permutations see [2].

The overlap-integral  $(\psi_n, \pi \psi_n)$  is of the form

$$I = \int dx \, dy_1 \, dy_2 \, \overline{\eta_n(x) \, \varphi_1(y_1) \, \varphi_2(y_2)} \, \eta_n(x') \, \varphi_1(y_1') \, \varphi_2(y_2'),$$

where x',  $y'_1$ ,  $y'_2$  are coordinates adapted to the decomposition  $(C'_1, C'_2)$ . We distinguish the regions

(1) 
$$|y_1| > R$$
 or  $|y_1'| > R$ 

(2) 
$$|y_2| > R$$
 or  $|y_2'| > R$ 

(3) 
$$|y_i| \le R$$
 and  $|y_i'| \le R$   $(i = 1, 2)$ ,

and denote the contribution of region (i) to I by  $I_i$ . By the Schwarz inequality,

$$|I_1| \leq 2 \left( \int_{|y_1| > R} dy_1 |\varphi_1(y_1)|^2 \right)^{1/2} \to 0$$

for  $R \to \infty$ , and similarly for  $I_2$ . For region (3) we shall prove below that

$$|x| \leqslant aR$$
 and  $|x'| \leqslant aR$  (11)

for some constant a depending only on the masses. Therefore

$$|I_3| \leqslant \int_{|x| \leqslant aR} dx |\eta_n(x)|^2 \leqslant aR \int dx |x|^{-1} |\eta_n(x)|^2$$
$$= aRn^{-2}$$

since  $(\eta_n, |x|^{-1}\eta_n) = n^{-2}$  [4]. By choosing first R and then n sufficiently large, we can make  $I_1 \ldots I_3$  arbitrarily small. Therefore, (10) is satisfied.

To prove (11), finally, we remark that  $(C'_1, C'_2)$  is obtained from  $(C_1, C_2)$  by exchanging groups  $g_i \subset C_i$  of an equal number of identical particles. Let m be the total mass of  $g_i$ . Then  $m < M_1$  or  $m < M_2$  since otherwise  $C_1$  and  $C_2$  would be identical, which is impossible because  $q_1q_2 < 0$ . Let  $z_i$  be the position of the CM of  $g_i$  with respect to the CM of  $C_i$ . Then the CM of  $C'_1$ ,  $C'_2$  have the following coordinates relative to the CM of  $C_1$ :

$$C_1': mM_1^{-1}(-z_1+x+z_2)$$

$$C_2'$$
:  $x + mM_2^{-1}(-z_2 - x + z_1)$ .

Taking the difference we get

$$x' = x(1 - \alpha) + \alpha(z_1 - z_2)$$

with  $\alpha = m(M_1^{-1} + M_2^{-1})$ ,  $0 < \alpha < 2$ . Now  $|y_i| \le R$  implies  $|z_i| \le bR$  for some b depending on the choice of the internal coordinates  $y_i$ . Therefore

$$|x'| \leqslant |x| |1 - \alpha| + 2\alpha bR.$$

By the same argument,

$$|x| \le |x'| |1 - \alpha| + 2\alpha bR$$
  
$$\le |x|(1 - \alpha)^2 + 2\alpha |1 - \alpha| bR + 2\alpha bR,$$

or, since  $(1-\alpha)^2 < 1$ ,

$$|x| \le [1 - (1 - \alpha)^2]^{-1}(|1 - \alpha| + 1) 2\alpha bR$$

and similarly for x'. This proves (11).

## References

- [1] W. Hunziker, Helv. Phys. Acta 39, 451 (1966).
- [2] B. SIMON, Helv. Phys. Acta 43, 607 (1970).
- [3] B. SIMON, Proc. A.M.S., 42, 395 (1974).
- [4] See, for example, E. U. CONDON and G. H. SHORTLEY, *Theory of Atomic Spectra* (Cambridge University Press 1957).
- [5] H. Bethe, Quantenmechanik der Ein- und Zwei-Elektronenprobleme, Handbuch der Physik XXIV/1, p. 287 (Springer Verlag, Berlin 1933).

# Notes added in proof

- 1. The spectrum of H in subspaces of given angular momentum, parity and symmetry under permutations of identical particles is discussed in E. Balslev, Annals of Physics 73, 49 (1972).
- 2. To derive (6) it suffices to have pointwise exponential bounds for the one-particle densities  $\rho_i$ . Such bounds have already been proved by J. M. Combes and L. Thomas, Commun. math. Phys. 34, 251 (1973).
- 3. The derivation of exponential bounds in subspaces of given symmetry presents some technical difficulties. These are discussed in W. Hunziker, O'Connors Theorem with Statistics, preprint 1975.
- 4. J. M. Combes and, independently, H. Tamura have obtained related results on the asymptotic behaviour of eigenvalues near the continuum (private communications by J. M. Combes and L. Thomas).