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On the Asymptotic Behaviour of Atomic Spectra near the Continuum

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Abstract. If Σ 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 Σ. Σ is the lowest threshold for break-up of the system into independent parts [1, 2].

b) If Σ is the threshold for break-up into two sub-systems C_1, C_2 with total charges q_1, q_2 such that $q_1 q_2 < 0$, then the number of eigenvalues below Σ 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 $(1 \ldots N)$:

$x \in R^3$ = 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 $\hbar = 1$, $q_1 q_2 = -2$, $M_1^{-1} + M_2^{-1} = 2$. 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 φ_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

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

of multiplicity n^2 with eigenfunctions

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

where η_n satisfies

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

We shall assume that η_n, φ_1, φ_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, ψ_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 φ_i [3].

2. Basic Inequalities

For real E and $a > 0$ let

$$N_a = \text{spectral subspace of } H \text{ where } (H - E)^2 \leqslant a^2. \tag{1}$$

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

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

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

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

If $E + \varepsilon < \Sigma$, we conclude that H possesses eigenvalues of total multiplicity $\geqslant \dim M$ 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

$$\|P\psi\| \geqslant \lambda \tag{5}$$

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

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

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 $\|(H-E_n)\psi_n\|$

$$\|(H-E_n)\,\psi_n\| = \|(V+2|x|^{-1})\,\psi_n\|$$
$$\leqslant \sum_{\substack{i\in C_1\\ k\in C_2}} |e_i e_k|\,\|U_{ik}\,\psi_n\|$$

with

$$U_{ik} = |\,|x-z_1+z_2|^{-1} - |x|^{-1}|$$
$$\leqslant |x|^{-1}|z_1-z_2|\,|x-z_1+z_2|^{-1},$$

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

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

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

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

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

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

the corresponding ψ_n then span a subspace M_n with

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

where $[a]$ = smallest integer $\geqslant a$. It follows from (6), (7) and (8) that for $\alpha \leqslant 4$

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

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

Theorem: There exists a constant C such that for $3 < \alpha \leqslant 4$ 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 $|x| \ll n^2$ 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 λ 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 ψ_n by a permutation π of identical particles which sends the partition (C_1, C_2) of $(1 \ldots N)$ 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) $|y_i| \leqslant R$ and $|y_i'| \leqslant R$ $(i = 1, 2)$,

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

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

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

$$|x| \leqslant aR \quad \text{and} \quad |x'| \leqslant aR \tag{11}$$

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 $q_1 q_2 < 0$. 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:

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

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

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 $|y_i| \leqslant R$ implies $|z_i| \leqslant bR$ 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,

$$\begin{aligned} |x| &\leqslant |x'|\,|1-\alpha| + 2\alpha bR \\ &\leqslant |x|(1-\alpha)^2 + 2\alpha|1-\alpha|\,bR + 2\alpha bR, \end{aligned}$$

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

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

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 ρ_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).