Fermilab Library
0 1160 0026494 9

UWThPh-1993-41
November 8, 1993

FERMILAB
DEC 30 1993
LIBRARY

Peculiar Effects from Number Theory for Doubly Excited Rydberg States of Two–Electron Ions

NAME | I.D No.
RETURN TO FERMILAB LIBRARY

B. Baumgartner
Institut für Theoretische Physik
Universität Wien

Abstract

Without electron repulsion there were accidental degeneracies between some of the excited states of two– (or more–) electron atoms among themselves and also with ionisation thresholds. The effects of these degeneracies on resonances of highly ionized atoms decaying by the Auger effect of autoionisation, are investigated by treating the repulsion between the electrons as a perturbation.

To appear in J. Phys. B.

1 Introduction

The states of the Helium atom or of an ion with two electrons can be considered as emerging from the states of the Hamiltonian

$$H_0 = -\frac{\hbar}{2m}(\Delta_1 + \Delta_2) - Z\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{1}$$

(non–relativistic and in the approximation of infinite nuclear mass) with independent electrons, perturbing with the repulsion

$$V = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}. \tag{2}$$

The eigenstates of H_0 with energies $-(1/n_1^2 + 1/n_2^2)$ hRy, $n_2 \geq n_1 \geq 3$ turn into resonances, metastable states decaying by autoionisation [Co]. With the closely related atoms of Barium these resonances have been observed with quantum number n_2 up to ~ 50 [Ab], [Ca], [WC] (and references therein).

The localisation of these resonances can be calculated by ordinary perturbation theory in first order. Higher orders can in principle be achieved after performing a complex dilation [ABC] (also called complex rotation [Ho1]). This complex dilation rotates the continuous spectrum of each channel into the complex plane, leaving only its ionisation threshold on the real axis, uncovering most of the excited states. The exposed bound states with $n_i \geq 3$ wander off into the complex plane when the perturbation is turned on, denoting the poles of resonances after reversing the complex dilation.

Since a real dilation $r \mapsto r/Z$, combined with a transformation of Hamiltonians and energies $H \mapsto H/Z^2$, allows to consider $1/Z$ as the coupling parameter for the perturbing repulsion, it is to be expected that perturbation theory is adequate for high Z. Examining detailed numerical calculations [Ho2], it seems that already the first order perturbation theory gives a qualitatively good picture of the real parts of the resonances down to $Z \sim 4$. So it is worthwhile to have a closer look on the perturbation theory and its prerequisites.

The first step in perturbation theory has to be the diagonalisation of V in the subspaces of eigenvectors of H_0 belonging to degenerate eigenvalues. In most cases these subspaces are characterized by two main quantum numbers n_1, n_2. Now comes the surprise: There are accidental degeneracies due to the existence of pairs $\{n_1, n_2\} \neq \{n_3, n_4\}$ with

$$\frac{1}{n_1^2} + \frac{1}{n_2^2} = \frac{1}{n_3^2} + \frac{1}{n_4^2}. \tag{3}$$

Moreover, in the limit $n_2 \to \infty$ the energies $\propto 1/n_1^2$ denote the ionisation edges, and there are also coincidences

$$\frac{1}{n_1^2} = \frac{1}{n_3^2} + \frac{1}{n_4^2}. \tag{4}$$

In the following we report about how to find these degeneracies, about the consequences they cause for the resonances, and about related cases.

2 Number theory to locate degeneracies

The accidental degeneracy (3) is equivalent to

$$(n_2 n_3 n_4)^2 + (n_1 n_3 n_4)^2 = (n_1 n_2 n_4)^2 + (n_1 n_2 n_3)^2. \tag{5}$$

On the other hand, given positive integers $z_1 \dots z_4$ with

$$z_1^2 + z_2^2 = z_3^2 + z_4^2, \tag{6}$$

the degeneracy (3) holds with the quantum numbers

$$n_i = \mathrm{Z}/z_i. \tag{7}$$

Z a common multiple of $z_1 \dots z_4$. So the present problem to determine the degeneracies is equivalent to the time honored question, which integers can be represented as a sum of two squares in more than one way.

One answer to this question, already known to Diophant, is found by way of the equality

$$(pq + rs)^2 + (ps - qr)^2 = (ps + qr)^2 + (pq - rs)^2. \tag{8}$$

All quadrupels $(z_1 \dots z_4)$ and hence all quadrupels $(n_1 \dots n_4)$ can be determined this way [Sh]. There are however no exact relations between the magnitudes of the various quadruples. An alternative way to determine all the accidental degeneracies below some negative energy E is to proceed numerically: For each $n_1 \leq (|E|/\mathrm{hRy})^{1/2}$ one has to test the finite set

$$\mathcal{M} := \{(n_3, n_4) : n_4 \geq n_3 > n_1, n_3^{-2} + n_4^{-2} \geq n_1^{-2}\} \tag{9}$$

whether $(n_4^{-2} + n_3^{-2} - n_1^{-2})^{-1/2}$ is an integer, and whether

$$n_3^{-2} + n_4^{-2} = n_3'^{-2} + n_4'^{-2} \tag{10}$$

for $(n_3', n_4') \neq (n_3, n_4)$.

The case $ps = qr$ in equ. (8) gives $z_2 = 0$ and a Pythagorean triplet

$$z_1^2 = z_3^2 + z_4^2 \tag{11}$$

corresponding to a coincidence (4) by setting

$$n_i = \mathrm{Z}/z_i. \tag{12}$$

The Pythagorean triplets $a^2 + b^2 = c^2$ correspond also to the special degeneracies (3) with $n_3 = n_4$ by setting

$$z_1 = a + b, \qquad z_2 = |a - b|, \qquad z_3 = z_4 = c. \tag{13}$$

The simplest Pythagorean triplet (3,4,5) gives in this way not only the lowest case of coincidence (4) with

$$(n_1; n_3, n_4) = (12; 15, 20), \tag{14}$$

but also the lowest degeneracy (3) with

$$(n_1 \dots n_4) = (5, 35; 7, 7). \tag{15}$$

We give in the table the lowest degeneracies.

n_1	n_2	n_3	n_4	$-E_0 = 1/n_1^2 + 1/n_2^2$
5	35	7	7	.040 816
5	90	6	9	.040 123
6	72	8	9	.027 971
7	56	8	14	.020 727
10	55	11	22	.010 331
10	70	14	14	.010 204
10	180	12	18	.010 031
10	1320	11	24	.010 001
12	144	16	18	.006 993
12	∞	15	20	.006 994

Table 1: The lowest degeneracies, the energies in hRy

3 The effect on the resonances: spectral repulsion

There exist definite algebraic relations between the hydrogenic states $|n, \ell, m\rangle$ and $|n \pm 1, \ell, m\rangle$ [Sch], which extend to relations between the eigenstates $|n_1, n_2, \underline{\beta}\rangle$ and $|n_1, n_2 \pm 1, \underline{\beta}\rangle$ of the unperturbed Hamiltonian H_0, ($\underline{\beta}$ denoting any set of necessary extra parameters). These algebraic relations should give some regularities in the matrix elements

$$V_{\underline{\beta},\underline{\gamma}} = \langle n_1, n_2, \underline{\beta}|V|n_1, n_2, \underline{\gamma}\rangle, \tag{16}$$

when considering changes of n_2 to $n_2 \pm 1$, implying further regularities in diagonalizing $(V_{\underline{\beta},\underline{\beta}})$ in the subspaces $\mathcal{H}_{n_1,n_2}$, and yielding finally regularities in first order perturbation theory, *as long as the exceptional degeneracies are ignored.* If there is a degeneracy (3), these regularities will be interrupted, because V has to be diagonalized in the "interaction subspace"

$$\mathcal{H}_{\text{int}} := \mathcal{H}_{n_1,n_2} \oplus \mathcal{H}_{n_3,n_4}, \tag{17}$$

spanned by all linear combinations of $|n_1, n_2, \underline{\beta}\rangle$ and $|n_3, n_4, \underline{\gamma}\rangle$. Applying the min–max–principle in the same way as is done in the Rayleigh–Ritz technique ([CH], XIII.1 and XIII.2 in [RS]), one gets strict inequalities between eigenvalues $\varepsilon_{\text{int},A,i}$ of the matrix V in the larger space $\mathcal{H}_{\text{int}}$ and the "regular" eigenvalues $\varepsilon_{n_1,n_2,A,j}$, $\varepsilon_{n_3,n_4,A,k}$ in the "regular" smaller subspaces. (Now we suppose A to denote the quantum numbers of multiplicity, total angular momentum and parity; i, j or k just numerating the eigenvalues.) We get the

Theorem of spectral repulsion:

$$\begin{aligned} \max_i \varepsilon_{\text{int},A,i} &\geq \max\left\{\max_j \varepsilon_{n_1,n_2,A,j}, \max_k \varepsilon_{n_3,n_4,A,k}\right\} \\ \min_i \varepsilon_{\text{int},A,i} &\leq \min\left\{\min_j \varepsilon_{n_1,n_2,A,j}, \min_k \varepsilon_{n_3,n_4,A,k}\right\} \end{aligned}$$

and, moreover, for

$$\begin{aligned} E_{\text{top}}(n_1, n_2, A, N) &:= \text{sum of the } N \text{ highest } \varepsilon_{n_1,n_2,A,j}, \\ E_{\text{bottom}}(n_1, n_2, A, N) &:= \text{sum of the } N \text{ lowest } \varepsilon_{n_1,n_2,A,j}: \end{aligned}$$

$$\begin{aligned} E_{\text{top}}(\text{int}, A, N) &\geq \max_{0\leq M\leq N} (E_{\text{top}}(n_1, n_2, A, M) + E_{\text{top}}(n_3, n_4, A, N-M)) \\ E_{\text{bottom}}(\text{int}, A, N) &\leq \min_{0\leq M\leq N} (E_{\text{bottom}}(n_1, n_2, A, M) + E_{\text{bottom}}(n_3, n_4, A, N-M)). \end{aligned}$$

In other words: The mean value of the N highest eigenvalues of V in the larger space $\mathcal{H}_{\text{int},A}$ is greater than the mean value of the highest elements in the union of the sets of eigenvalues of V in $\mathcal{H}_{n_1,n_2,A}$ and in $\mathcal{H}_{n_3,n_4,A}$. For the N lowest eigenvalues the converse inequality holds.

The proof follows from the variational principle by which the left hand sides of the inequalities above are given by an extremum over the set of N orthogonal unit-vectors of $\mathcal{H}_{\text{int},A}$, whereas the right hand sides are given by an extremum over a smaller set, where linear combinations of vectors $|n_1, n_2, \underline{\beta}\rangle$ with $|n_3, n_4, \underline{\gamma}\rangle$ are excluded.

The sum (or the mean value) of all the iegnvalues however remains unchanged: It is equal to the trace of V in the space $\mathcal{H}_{\text{int},A}$, independent of the chosen basis, and equal to the sum of the traces in the subspaces $\mathcal{H}_{n_1,n_2,A}$ and $\mathcal{H}_{n_3,n_4,A}$.

The same is true for the widths $\Gamma/2$ of the resonances, as they are calculated by Fermi's golden rule. This rule can be written as (see 4.4,13 in [Th])

$$\frac{\Gamma}{2} = -\frac{\pi}{Z^2}\langle n_1, n_2, A, j|F|n_1, n_2, A, j\rangle, \tag{18}$$

$$F = \frac{1}{r_{12}} P_\perp \delta(H_0 - E_0) P_\perp \frac{1}{r_{12}}, \tag{19}$$

$P_\perp$ being the projection onto the channels with continuous spectrum at E_0.

This fact can be stated as the

Invariance of the mean value: In first order perturbation theory the mean value of the real parts, emerging from a degenerate eigenvalue, and belonging to states with some fixed type ${}^xL^\pm$ will be the same, and also in second order perturbation theory the mean value of the imaginary parts of the resonance-poles will be the same, the interaction between the subspaces being ignored or not.

Concerning the coincidence (4) of an eigenvalue with an ionisation threshold, there appears the fundamental problem to prove the conversion of the eigenvalue to resonances. The coincidence remains after complex dilation, and perturbation theory cannot be applied. Only formally one can calculate the change of the eigenvalue (to first order in $1/Z$), given by the expectation value of $1/r_{12}$, and also the appearance of an imaginary part (in second order), given by Fermi's golden rule. This problem will be discussed elsewhere.

4 Heuristic discussion of the effect

To be precise, we choose $A = {}^1S^e$ states emerging from $\mathcal{H}_{5,35;7,7}$: The subspace $\mathcal{H}_{5,35,A}$ is five-dimensional, $\mathcal{H}_{7,7,A}$ is seven-dimensional. By considering the virial theorem for the hydrogen atom,

$$\left\langle \frac{1}{r} \right\rangle_n = 2|E| \propto \frac{1}{n^2}, \tag{20}$$

and estimating the eigenvalues of $1/r_{12}$ in $\mathcal{H}_{n_1,n_2}$ roughly to be comparable to $\langle 1/r\rangle_{n_2}$, we estimate the eigenvalues of $1/r_{12}$ in $\mathcal{H}_{7,7}$ to be about twenty times as big as the eigenvalues in

$\mathcal{H}_{5,35}$. By ignoring the interaction between the spaces, one would get two well separated bunchs of energies: Five lower ones belonging to (5,35), seven higher ones belonging to (7,7).

The "interaction", the matrix elements of $1/r_{12}$ connecting the subspaces and effecting a configuration mixing, will certainly be much smaller than the matrix elements in $\mathcal{H}_{7,7}$. So we guess that there will remain two well separated bunchs of energies, the 7 higher ones not much changed. The effect of configuration mixing on the five smaller ones however may be appreciably, in magnitude comparable to their distance from the unperturbed energy.

Concerning the observability, we remark that the distances between resonances vary as $1/Z$, their widths as $1/Z^2$. The ratio distance/width is proportional Z, and the resonance peaks $(5, n_2)$ with $n_2 \sim 35$ should be well separated for $Z \sim 10$. Effects of spin-orbit coupling are estimated as proportional to Z^4/n^3 and can be ignored.

5 Related cases

Coincidence of spectral lines. Changing (3) to

$$\frac{1}{n_1^2} - \frac{1}{n_3^2} = \frac{1}{n_4^2} - \frac{1}{n_2^2}, \tag{21a}$$

$$\frac{1}{n_1^2} - \frac{1}{n_4^2} = \frac{1}{n_3^2} - \frac{1}{n_2^2}. \tag{21b}$$

One has a relation of each degeneracy (3) to two or (in case $n_3 = n_4$) one coincidence of lines in the hydrogen spectrum, a possibility which has only recently been discovered [WW].

Changing (4) to

$$\frac{1}{n_1^2} - \frac{1}{n_3^2} = \frac{1}{n_4^2}, \tag{22a}$$

$$\frac{1}{n_1^2} - \frac{1}{n_4^2} = \frac{1}{n_3^2}, \tag{22b}$$

one has a relation of each coincidence (4) to two coincidences of spectral lines with an ionisation threshold.

Multiple degeneracies. There exist integers, which can be represented as a sum of squares not only in two, but in three different ways. The same is true, with two replaced by four, or any number. The related degeneracies of sums of inverse squares will involve very high quantum numbers and will probably remain unobservable.

Multiply excited Rydberg states. Just by adding $1/n_5^2$ to both sides of equation (3), one gets degeneracies of triply excited states. There exist also triples of completely different numbers with the same sum of inverse squares. The same is true for higher multiples. The effects in these cases will be the same as discussed above for doubly excited states.

References

[Ab] M. Abutaleb et al.: $6p_{1/2}, p_{3/2}$ nf $J = 1 - 5$ autoionizing series of barium, Phys. Rev. A44, 4187–4202 (1991)

[ABC] J. Aguilar and J.M. Combes: A class of analytic perturbations for one–body Schrödinger Hamiltonians, Commun. Math. Phys. 22, 269–279 (1971)
E. Balslev and J.M. Combes: Spectral properties of many–body Schrödinger operators with dilation–analytic interactions, Commun. Math. Phys. 22, 280–294 (1971)

[Ca] P. Camus et al.: Spectroscopic studies of 9dn'd doubly excited autoionising states of neutral barium, J. Phys. B18, L481–L487 (1984)

[CH] R. Courant, D. Hilbert: Methoden der Mathematischen Physik I, Springer Verlag Berlin–Heidelberg–New York 1968

[Co] R.D. Cowan: The Theory of Atomic Structure and Spectra, University of California press 1981

[Ho1] Y.K. Ho: The method of complex coordinate rotation and its applications to atomic collision processes. Phys. Rep. 99, 1–68 (1983)

[Ho2] Y.K. Ho: Complex–coordinate calculations for doubly excited states of two–electron atoms, Phys. Rev. A23, 2137–49 (1981)
Y.K. Ho: Complex–coordinate calculation of ^{1,3}D resonances in two–electron systems, Phys. Rev. A44, 2895–99 (1991)
Y.K. Ho and A.K. Bhatia: Doubly excited $^{1,3}P^e$ states in heliumlike systems, Phys. Rev. A47, 2628–33 (1993)

[RS] M. Reed, B. Simon: Methods of Modern Mathematical Physics, IV: Analysis of Operators, Academic Press, New York, San Francisco, London 1970

[Sch] E. Schrödinger: A Medhod of Determining Quantum Mechanical Eigenvalues and Eigenfunctions, Proc. R.I.A., Vol. XLVI, Sect A, 9–16 (1940)

[Sh] D. Shanks: Solved and Unsolved Problems in Number Theory, Spartan Books, Washington, D.C., 1962

[Th] W. Thirring: A Course in Mathematical Physics 3, Quantum Mechanics of Atoms and Molecules, Springer Verlag New York, Wien 1981

[WC] X. Wang, W.E. Cooke: 7sng autoionizing states of barium, Phys. Rev. A47, 1778–82 (1993)

[WW] D.W. Wyss, W. Wyss: Coincidental spectral lines for the Hydrogen spectrum, Found. Phys. 23, 465–468 (1993)