LETTER TO THE EDITOR

Perturbation of Rydberg series by atomic compound states

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Abstract. The discrete spectrum of excited states of an atom contains Rydberg series of states and valence excited states, made up of electron orbitals with small principal quantum numbers. For an atom with a few electrons in the open outer shell the spectrum of the valence excited states is extremely dense and extremely complicated, and the corresponding atomic eigenstates are strongly chaotic and similar to nuclear compound states. This enables us to consider mixing of the Rydberg and compound valence atomic states in a general form as a function of the residual interaction strength. It appears that the mixing reaches its maximum for the 'physical' values of the interaction. The Rydberg series are strongly perturbed for $n < D^{-1/3}$, where D is the mean level spacing between the compound states (in atomic units). For larger values of n the mixing is weak for any interaction strength. This follows from the separable character of the interaction between the Rydberg and compound states.

As is known the discrete excitation spectra of most atoms contain two distinctly different types of states: Rydberg states and so-called 'valence' states. In the Rydberg states one of the electrons has a large principal quantum number n. The Rydberg states are characterized by large orbital radii $r \propto n^2$. Their energy spectrum is regular and is characterized by the quantum defect μ, $E_n \simeq -1/2(n-\mu)^2$ (atomic units are used throughout). The density of the Rydberg states ρ_n goes to infinity at the ionization threshold, $\rho_n = D_n^{-1}$, where $D_n \simeq 1/n^3$ is the mean level spacing between Rydberg states. In contrast, the atomic valence states are built up of several excited electrons with small principal quantum numbers. Unlike the Rydberg states, they have small radii of about a few Bohr radii (this difference has been used by experimentalists to discern Rydberg states among valence states in lanthanides and actinides [1, 2]). The energy spacing between the valence states fluctuates strongly with respect to its mean value D. The density of the valence excited states $\rho = 1/D$ is finite but increases rapidly with energy. As a result, the spectra of heavy open-shell atoms are enormously complex.

The study of Rydberg series has important applications. Experimentally, it provides a highly accurate method for measuring ionization limits of atoms. Due to the high density of the valence states the procedure of assigning Rydberg series in complex atoms becomes extremely difficult. For example, near the ionization threshold of U the observed level density of Rydberg and valence states was $\rho \sim 10^3$ eV^{-1} [1], and the experimentalists could identify the Rydberg states only for $\nu > 36$ ($\nu = n - \mu$).

The aim of this work is to estimate how strong the perturbation of the Rydberg series is in a situation when the spectrum of valence excited states is dense. Of course, even in the most complex spectra there are Rydberg series converging to the ionization limit. The questions

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we want to answer are: at which n do the Rydberg states become 'visible'? How does the mixing between the Rydberg and valence states depend on the strength of the residual interaction? Can this interaction mix the two manifolds completely, thus eliminating the Rydberg states in some part of the spectrum? We show in this paper that for $D_n < D$, i.e. for $n > D^{-1/3}$, there is almost no mixing between the manifolds for any residual interaction strength. This result is a consequence of a separable form of the interaction between the two level manifolds. Curiously, it appears that the state mixing is maximal for the 'physical' strength of the interaction.

It has been shown in [3] that simultaneous excitation of several valence electrons in a rare-earth atom (Ce) produces a dense spectrum of *compound* valence atomic states. Using a configuration-interaction approach the atomic eigenstates

$$|i\rangle = \sum_j C_j |\Phi_j\rangle \qquad \left(\sum_j C_j^2 = 1\right) \tag{1}$$

are obtained by diagonalizing the Hamiltonian matrix $H_{jj'} \equiv \langle\Phi_j|H|\Phi_{j'}\rangle$. The basis states $|\Phi_j\rangle$ possess the exact angular momentum and parity J^π and correspond to various electron configurations. The coefficients C_j describe mixing of the basis states by the residual Coulomb interaction. The number of basis states formed by distributing several electrons among a few open orbitals is large (for pure combinatorial reasons), and the mean level spacing D between such states is small ($\lesssim 0.01$ eV). In this situation the basis states are strongly mixed by the perturbation, and each of the eigenstates is a superposition of a large number of basis states. This strong mixing takes place within a certain energy range $\Gamma_{\rm spr}$ called the spreading width. The value of $\Gamma_{\rm spr} \sim 2$ eV [3] can be used to estimate the number N of principal components, i.e. those C_j which contribute noticeably to the sum (1), $N \sim \Gamma_{\rm spr}/D \sim 100$. The principal components C_j have typical values $|C_j| \sim 1/\sqrt{N}$. Their statistics is close to that of independent random variables and becomes Gaussian when the mixing is complete. The properties described above make atomic valence excited states similar to nuclear compound states [4] and allow one to talk about many-body quantum chaos in complex atoms.

Spectral properties of compound states in nuclei were successfully modelled using ensembles of random matrices and, in particular, the Gaussian orthogonal ensemble (GOE, see, e.g., [5]). Energy level statistics in complex atomic spectra were also compared with the predictions of the GOE model [6, 7] and good agreement was found. As such the energy level statistics do not carry much information about the structure of the corresponding wavefunctions. The latter can be probed either directly, in numerical calculations, or through studying amplitudes or probabilities of transitions involving compound states.

In [8] statistical properties of the Coulomb matrix elements W coupling atomic compound states to the continuum were studied for Ce. The probability density of these matrix elements turned out to be almost Gaussian. This statistics corresponds to the Porter–Thomas distribution of the widths $\gamma = 2\pi|W|^2$ of these states. The distribution of the $E1$ amplitudes involving the compound states was also close to a Gaussian. Earlier evidence for this statistics can be found in the calculations of the dipole excitations in complex atoms [9]. Therefore, it appears that compound atomic eigenstates do indeed have a chaotic structure. This is the origin of the difficulties that one encounters in trying to calculate such eigenstates precisely (it is manifested as an extremely strong sensitivity of the result to the size of the configuration matrix, choice of single-electron orbitals, etc†). On the other hand,

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† This sensitivity, or 'enhancement of small perturbations' in quantum chaotic systems can be viewed as an analogue of the exponential divergence of trajectories in classical chaotic systems [10].

the chaotic structure enables one to use statistical methods for estimating matrix elements involving compound states. Hence, the problem of perturbation of the Rydberg series by the compound states can be addressed in a general form.

Let us consider an atom with several electrons in the open valence shell(s) (e.g. a rare-earth atom). Suppose that the Hamiltonian of the valence electrons in the field of the core has been diagonalized separately within the subspaces of the valence states and Rydberg states of the same symmetry J^π. As a result we have compound (valence) atomic eigenstates $|i\rangle$ with energies E_i and Rydberg states $|n\rangle$ with energies E_n†. Now we will consider their interaction. In the basis of $|i\rangle$ and $|n\rangle$ states the Hamiltonian matrix looks like

$$H = \left(\begin{array}{c|c} H_{ii'} & H_{in} \\ \hline H_{ni} & H_{nn'} \end{array} \right) \tag{2}$$

where $H_{ii'} = \delta_{ii'} E_i$ and $H_{nn'} = \delta_{nn'} E_n$ are diagonal, and $H_{in} = \langle i|W|n\rangle$ mixes the Rydberg and compound states through the Coulomb interaction W between the valence electrons. Due to the small radius of the compound state i the matrix element $\langle i|W|n\rangle$ is determined by the behaviour of the Rydberg state orbital at small distances, $\varphi_n(r) \simeq n^{-3/2}\varphi(r)$. Hence, the following important scaling property:

$$\langle n|W|i\rangle \simeq n^{-3/2}\langle n_0|W|i\rangle \tag{3}$$

where n_0 is the effective lowest member of the Rydberg series, a simple valence-like state. Note that the true scaling factor is $\nu^{-3/2}$, but we neglect any difference between n and $\nu = n - \mu$ hereafter.

The matrix element $\langle n_0|W|i\rangle$ can be estimated similarly to matrix elements involving nuclear compound states [11],

$$\langle n_0|W|i\rangle = \sum_j \langle n_0|W|\Phi_j\rangle C_j \sim \frac{\sqrt{q}M}{\sqrt{N}} \tag{4}$$

where M is a typical two-body Coulomb matrix element between different valence orbitals, q is the number of nonzero items in the sum, which depends on the number of valence orbitals involved (say, $q \sim 10$), and $\sqrt{q}$ is a root-mean-square estimate due to the randomness of C_j.

Let us now estimate the admixture of a compound state to a Rydberg state by perturbations. Combining (3) and (4) one obtains

$$\frac{\langle i|W|n\rangle}{E_i - E_n} \simeq \frac{\sqrt{q}M}{\sqrt{N}n^{3/2}D} \tag{5}$$

where we put $|E_i - E_n| \sim D$ as for the typical distance from the Rydberg state to a nearby compound state, since, of course, mixing of closely spaced levels should be the strongest. Using $D \sim \Gamma_{\mathrm{spr}}/N$ and $D_n = n^{-3}$ we can rewrite (5) as

$$\frac{\langle i|W|n\rangle}{E_n - E_i} \simeq \frac{\sqrt{q}M}{\sqrt{\Gamma_{\mathrm{spr}}}} \sqrt{\frac{D}{D_n}} . \tag{6}$$

In the same manner the estimate of the admixture of a nearby Rydberg state to the compound state can be obtained:

$$\frac{\langle n|W|i\rangle}{E_i - E_n} \sim \frac{\sqrt{q}M}{\sqrt{\Gamma_{\mathrm{spr}}}} \sqrt{\frac{D_n}{D}} \tag{7}$$

where $|E_n - E_i| \sim D_n$ has been used.

† For simplicity we consider a single Rydberg series.

The mixing between the Rydberg and compound states is strong when the right-hand sides of (7) and (6) are comparable to unity. Our numerical calculations for Ce [8] suggest that

$$M\sqrt{q}/\sqrt{\Gamma_{\mathrm{spr}}} \sim 1 \tag{8}$$

corresponds to the 'physical' strength of the residual interaction. This relation can be considered as a manifestation of the 'golden rule' $\Gamma_{\mathrm{spr}} \sim 2\pi |M|^2\rho$, where $\rho \sim 1$ is the single-particle valence level density. Thus, estimates (6) and (7) depend on $\sqrt{D_n/D}$ only. It follows from (6) that for $D < D_n$ ($n < D^{-1/3}$) the Rydberg states are strongly perturbed, whereas for $D_n < D$ ($n > D^{-1/3}$) the admixture of the compound states to the Rydberg states becomes small, and the Rydberg series is weakly perturbed. It should be *vice versa* for the compound states.

If, for some reason, the residual interaction between the Rydberg and compound states is smaller than what we infer from the calculations for Ce, the weakly perturbed Rydberg series can be seen for lower values of n. What happens in the opposite case of a stronger residual interaction? Can it substantially perturb the Rydberg states for arbitrarily large n?

To answer this question we note that the interaction between the Rydberg and compound states (3) is separable, i.e. $H_{in} = \lambda W_i B_n$, where $\lambda W_i = \langle i|W|n_0 \rangle$ and $B_n = \sqrt{D_n}$, and we introduced the parameter λ to characterize the strength of the compound Rydberg mixing. For this Hamiltonian one can explicitly calculate the eigenvector $|E\rangle = \sum_i C_i|i\rangle + \sum_n C_n|n\rangle$,

$$C_i = \frac{\lambda W_i F}{E - E_i} \qquad C_n = \frac{B_n G}{E - E_n} \tag{9}$$

where $F = \sum_m B_m C_m$, and $G = \lambda \sum_i W_i C_i$. G and F satisfy the equations

$$G = \lambda^2 F \sum_i \frac{W_i^2}{E - E_i} \qquad F = G \sum_n \frac{B_n^2}{E - E_n} \tag{10}$$

which yield the equation for the energy E,

$$\lambda^2 \sum_i \frac{W_i^2}{E - E_i} \sum_n \frac{D_n}{E - E_n} = 1. \tag{11}$$

If the strength of the residual interaction increases ($\lambda \to \infty$), this equation becomes

$$\sum_i \frac{W_i^2}{E - E_i} \sum_n \frac{D_n}{E - E_n} = 0. \tag{12}$$

In this case $\sum_i W_i^2/(E - E_i) = 0$ ($C_n = 0$) determines the new positions of the compound states and $\sum_n D_n/(E - E_n) = 0$ ($C_i = 0$) yields the new energies of the Rydberg levels. Thus, for the strong residual interaction there is no mixing between the compound and Rydberg states†. Since there is no mixing for both weak ($\lambda \to 0$) and strong ($\lambda \to \infty$) residual interactions, a critical value λ_c corresponding to the strongest mixing can be found.

To define λ properly let us use the fact that the matrix elements $\langle i|W|n_0 \rangle = \lambda W_i$ have Gaussian statistics. Then one can consider W_i for different compound states i as normally distributed independent Gaussian random variables, $\overline{W_i} = 0$, $\overline{W_i^2} = 1$. Consider the most interesting energy region where the two level manifolds have similar densities, $D_n \approx D$. The perturbative admixture is given by $\langle i|W|n \rangle/(E_i - E_n) \sim n^{-3/2}\langle i|W|n_0 \rangle/(D/2)$, where

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† A similar cross-over between the two regimes was recently discussed in relation to the problem of crossing of two bands of potential curves [12], when the interaction matrix was chosen in a separable form.

$D/2$ is the average level spacing in this part of the spectrum. Comparing this admixture with unity we obtain

$$\lambda_c \approx 0.5\sqrt{D}. \tag{13}$$

It is interesting that the real 'physical' strength of the residual interaction $\lambda_{\text{phys}} \sim \sqrt{q}M/\sqrt{N}$ (equations (4) and (8)) corresponds to $\lambda_{\text{phys}} \sim \lambda_c$.

To illustrate the dependence of the Rydberg compound mixing on the residual interaction strength, model calculations have been carried out. We consider a series of $N_R = 50$ Rydberg states, $E_n = -1/2n^2$, interacting with $N_C = 400$ compound states. The Hamiltonian matrix H has the form (2). To generate a realistic fluctuating spectrum of the compound states we used $H_{ii'} = E_i\delta_{ii'} + V_{ii'}$, where E_i are equally spaced between -0.08 and 0.02 au with $D = 2.5 \times 10^{-4}$ au, and $V_{ii'}$ is the Gaussian orthogonal random matrix. The matrix elements $V_{ii'} = V_{i'i}$ are chosen as independent Gaussian random numbers with zero mean and $\overline{V_{ii'}^2} = 4D^2$ ($|V_{ii'}| > D$ ensures strong mixing of the basis states within the compound state subspace). The matrix elements H_{in} which mix the compound and Rydberg states are taken as $H_{ni} = H_{in} = \lambda W_i n^{-3/2}$, where W_i are normal Gaussian random variables. Diagonalizing the Hamiltonian we obtain the eigenvalues $E^{(k)}$ and eigenvectors $(C_i^{(k)}, C_n^{(k)})$ of the problem.

To see the extent of mixing of the Rydberg and compound states we calculate the mean radius $\langle r \rangle$ of the eigenstates. This physical characteristic is used in experiments to distinguish the Rydberg states from the valence states. In the unperturbed basis the operator r is defined by its matrix elements, $r_{ii} = 1$, $r_{nn} = n^2$, $r_{ii'} = r_{nn'} = r_{in} = 0$. Thus, for the pure compound valence state the radius is unity, and for the nth unperturbed Rydberg state it is n^2. Figure 1 shows the dependence of the mean radii of the eigenstates

$$\langle r \rangle_k = \sum_i r_{ii}|C_i^{(k)}|^2 + \sum_n r_{nn}|C_n^{(k)}|^2 \tag{14}$$

on their binding energies $|E^{(k)}|$ for several values of λ.

For the given value of D we expect the maximal mixing to occur at $\lambda \sim \lambda_c \approx 0.008$. At this λ the Rydberg states must be strongly perturbed for $n < D^{-1/3} \approx 16$. For both smaller and larger values of λ the mixing between the Rydberg and compound states is weaker. Figure 1(a)–(c) correspond to the under-critical, critical and over-critical values of $\lambda = 0.0001$, 0.008 and 0.1, respectively. The dependence of mixing on the strength of the residual interaction λ is in good agreement with what we expected from the estimates made above. For both small and large λ the Rydberg series is almost unperturbed. Few compound states display sizeable admixtures of the Rydberg states. This happens due to approximate sporadic degeneracy resulting in small energy denominators. For the critical strength we do indeed observe strong mixing of almost all Rydberg states up to $n = 16$.

We have considered the perturbation of a Rydberg series by the compound valence atomic states in a complex open-shell atom. The chaotic structure of the compound states enables one to make statistical estimates of the matrix elements. It has been shown both analytically and numerically that the Rydberg series is strongly perturbed for $n < D^{-1/3}$ for the 'physical' values of the residual interaction between the Rydberg and compound states. Curiously enough, the 'physical' strength of the interaction gives rise to the strongest possible level mixing in this system. For larger values of n the mixing is weak for any value of the interaction strength. This property, as well as the existence of maximal mixing, is a consequence of the separable form of the interaction between the diffuse Rydberg and compact compound states. Our results can be used as a criterion for observing Rydberg
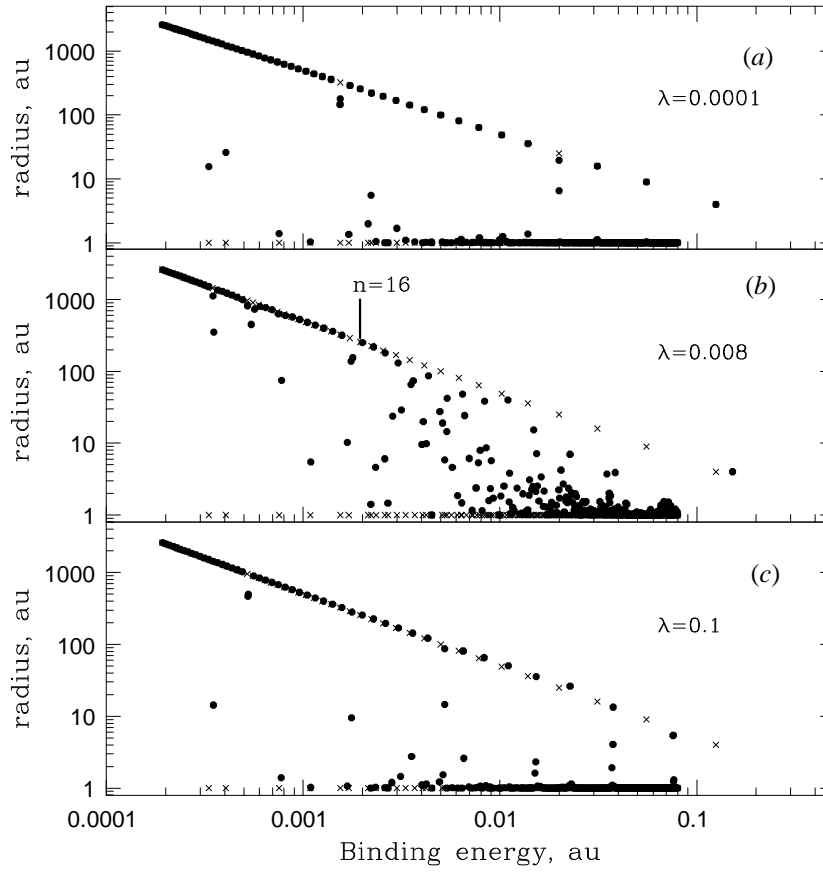
Figure 1. Dependence of the mean radius $\langle r \rangle$ of the eigenstates on the binding energy (●). The eigenstates of the model Hamiltonian are mixtures of the Rydberg and compound states. The magnitude of the mixing interaction is characterized by λ. Positions of unperturbed levels ($\lambda = 0$) are shown by crosses. (*a*) Weak, $\lambda = 0.0001$. (*b*) Critical, $\lambda = 0.008$. (*c*) Strong, $\lambda = 0.1$.

states. They also suggest an interpretation of the experimental results of [1, 2]. For example, the fact that only Rydberg states with $n > 36$ have been observed in U means that the level spacing between the compound (valence) states in this atom is $D \sim n^{-3} \sim 5$ cm^{-1} near the ionization threshold.

Estimates similar to (4) can be used to compare radiative lifetimes of the Rydberg and compound states. These lifetimes are important when a delayed ionization pulse technique is used to identify Rydberg states. The rough estimates $\tau_n \propto n^3$, $\tau_{\text{comp}} \propto N \sim \Gamma_{\text{spr}}/D$ can be expected for the Rydberg and compound states, respectively. Hence, $\tau_n > \tau_{\text{comp}}$ is achieved for $n^3 > 1/D$. This inequality coincides with the condition of weak perturbation of the Rydberg states.

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