

Chapter 1: Quantum Defect Theory

I. THE HYDROGEN ATOM

Rydberg atoms are excited states of atoms with a large principle quantum number, where the Rydberg electron is only weakly bound to the ionic core. This weak binding makes Rydberg atoms very sensitive to external perturbations and results in a wide range of unique features. To understand the basic properties of Rydberg atoms, it is instructive to first look at the solution of the hydrogen atom. In atomic units, the Hamiltonian is given by

$$H = \frac{\mathbf{p}^2}{2\mu} - \frac{1}{r}, \quad (1)$$

where position and momentum operators are canonically conjugated and $\mu = 1 - 1/m_p$ is the reduced mass according to the proton mass $m_p \approx 1836$. To solve the hydrogen problem, we first introduce the angular momentum operators

$$L_i = \varepsilon_{ijk} x_j p_k \quad (2)$$

and its square $L^2 = L_x^2 + L_y^2 + L_z^2$. Then, we can write the Hamiltonian as

$$H = \frac{p_r^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{1}{r}. \quad (3)$$

The angular momentum part can be solved independently from the radial part, using the angular momentum algebra. The eigenvalues of L^2 are given by $l(l+1)$, with l being a non-negative integer. Each eigenvalue of L^2 is $2l+1$ -fold degenerate. This degenerate manifold can be expressed in terms of eigenvectors of L_z , having integer eigenvalues m with $|m| \leq l$.

The radial part can be solved by expressing the radial momentum term in its coordinate representation, resulting in

$$H = -\frac{1}{2\mu r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{2\mu r} - \frac{1}{r}. \quad (4)$$

The resulting Schrödinger equation can then be solved using standard techniques [1]. We then obtain the solution

$$\psi(r) = \sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \exp(-r/na_0^*) (2r/na_0^*)^l L_{n-l-1}^{2l+1}(2r/na_0^*), \quad (5)$$

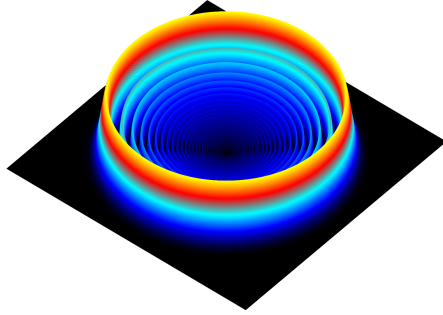


FIG. 1: Probability distribution of a Rydberg atom in the $35s$ state of hydrogen.

where n is the principal quantum number and $a_0^* = m_p/(m_p - 1)$ is the reduced Bohr radius. The associated Laguerre polynomials are normalized according to

$$L_{n-1}^1(0) = (n-1)!. \quad (6)$$

The eigenvalues do not depend on l , a fact that follows from the conservation of the Runge-Lenz vector, and are given by

$$E_n = -\frac{1}{2\mu n^2}. \quad (7)$$

Rydberg states are atomic excitation with a large principal quantum number n . We can call n being large if the properties of the Rydberg state are drastically different from the ground state. For practical purposes, this usually means $n \gtrsim 10$. For example, consider the expectation value of the radius r [2],

$$\langle r \rangle = \frac{a_0^*}{2} [3n^2 - l(l+1)]. \quad (8)$$

Already at relatively modest values of n , the spatial extension of the Rydberg state is already orders of magnitude larger than that of the ground state, see Fig. 1. Such an enhanced scaling with the principal quantum number n is characteristic for Rydberg states and leads to strongly exaggerated properties of Rydberg atoms. We will see many examples of such a scaling in the following.

II. QUANTUM DEFECT

Of course, we are not only interested in the properties of hydrogen atoms. However, for Rydberg states with a single excited electron, the eigenenergies can be well described by

l	$\delta_l[3]$
0	3.13
1	2.64
2	1.35
3	0.016
> 3	0

TABLE I: Quantum defect in Rb.

a simple phenomenological extension of the expression for hydrogen, as was first noted by Rydberg himself [4]. This can be done by introducing a "quantum defect" δ_l that depends (in leading order) only on the angular momentum quantum number, yielding

$$E_n = -\frac{1}{2\mu(n - \delta_l)^2}. \quad (9)$$

The quantum defect accounts for the corrections to the Coulomb potential by the core electrons. We can introduce an effective quantum number $n^* = n - \delta_l$. Already on the basis of the hydrogen wave functions we see that the probability to find the Rydberg electron within the core decreases with l , therefore the quantum defect should also decrease with l . Using laser spectroscopy, the eigenenergies of atoms can be measured very accurately, and as an example, the quantum defect for rubidium is shown in Tab. 1. For $l > 3$, the eigenstates are essentially hydrogenic. Experimentally, the quantum defect can be measured with much higher accuracy up to a relative uncertainty of 10^{-7} [5], but requires the treatment of the electron spin and introducing an n -dependence of the quantum defect.

However, it is evident that the Hamiltonian has to be modified to yield the desired eigenvalues. The easiest way to achieve this is to add an additional term $V_{eff}(r)$ to the radial part such that

$$\frac{l(l+1)}{2\mu r} + V_{eff}(r) = \frac{l^*(l^*+1)}{2\mu r}, \quad (10)$$

where the effective quantum number l^* is given by

$$l^* = l - \delta(l) + I(l) \quad (11)$$

with $I(l)$ being an integer [6]. The radial eigenfunction can then be expressed using an

extension of the associated Laguerre polynomials for non-integer $\alpha = 2l^* - 1$,

$$L_n^\alpha(\rho) = \sum_{p=0}^n (-\rho)^p \frac{\Gamma(n + \alpha + 1)}{p! \Gamma(p + \alpha + 1) \Gamma(n - p + 1)}. \quad (12)$$

Then, we obtain for the radial eigenfunctions

$$\psi_{n^*l^*}(r) = \sqrt{\left(\frac{2}{n^*}\right)^3 \frac{\Gamma(n - l - I)}{2n\Gamma(n^* + l^* + 1)}} \exp(-r/n^*a_0^*) (r/n^*a_0^*)^{l^*} L_{n-l-I-1}^{2l^*+1}(r/n^*a_0^*). \quad (13)$$

Note the different normalization factor compared to the hydrogen case due to the different definition of the associated Laguerre polynomials. The value of the integer I can be fixed by an appropriate choice of the number of nodes, $n - l - I - 1$, e.g., the ground state should not have any nodes. Alternatively, it is possible to improve the wave functions by choosing I such that transition matrix elements $\langle n', l' | x | n^*, l^* \rangle$ to match experimentally observed values [6].

III. POLARIZABILITY OF RYDBERG STATES

One important property of quantum defect theory is that the scaling relations we already saw in the hydrogen case remain valid, with the principal quantum number n being replaced by n^* . The key difference is that the l degeneracy found in the hydrogen atom is lifted. This means that we no longer have atoms with a permanent electric dipole moment (linear Stark effect) [14], but induced dipole moments (quadratic Stark effect). The strength of the quadratic Stark shift is captured in the polarizability α , according to

$$\Delta E = -\frac{1}{2}\alpha E^2, \quad (14)$$

where ΔE is the energy shift from the Stark effect and E is the applied electric field. Within the electric dipole approximation, the perturbation from the electric field is given by the Hamiltonian $H' = -dE$, where d is the electric dipole operator. In second order perturbation theory, we obtain for the Stark shift

$$\Delta E = \sum_{n'l'm'} \frac{\langle \psi_{nlm} | d | \psi_{n'l'm'} \rangle \langle \psi_{n'l'm'} | d | \psi_{nlm} \rangle}{E_{nl} - E_{n'l'}} E^2. \quad (15)$$

Using this expression, we can identify the polarizability as

$$\alpha = 2 \sum_{n'l'm'} \frac{|\langle \psi_{n'l'm'} | d | \psi_{nlm} \rangle|^2}{E_{n'l'} - E_{nl}}. \quad (16)$$

Note that while the polarizability is always positive for the ground state (since $E_{n'l'} > E_{nl}$), the polarizability of Rydberg states can actually be negative.

We are now interested in the scaling behavior of the polarizability with the effective quantum number n^* . For this, we first assume that the main contribution to the polarizability comes from the coupling to a single state, namely the one which is closest in energy for any dipole-allowed transition (i.e., $l' = l \pm 1$). The matrix element $\langle \psi_{n'l'm'} | d | \psi_{nlm} \rangle$ is proportional to a length and therefore has the same scaling as the expectation value for the orbital radius, $\langle r \rangle \sim n^{*2}$. The scaling for the energy difference in the denominator can be calculated as

$$\lim_{n \rightarrow \infty} E_{n,l+1} - E_{nl} = \lim_{n^* \rightarrow \infty} \frac{1}{2n^{*2}} - \frac{1}{2(n^* + \varepsilon)^2} = \varepsilon n^{*-3}. \quad (17)$$

If we combine these two scaling relations, we obtain for the polarizability an asymptotic behavior according to $\alpha \sim n^{*7}$. This dramatic scaling with the seventh power of the principal quantum number makes Rydberg atoms very sensitive to external electric fields and therefore very good candidates for the realization of electric field sensors.

If one wants to go beyond simple scaling relations, it is often appropriate to use semiclassical approximations for the dipole matrix element [7]. This allows to express the dipole matrix elements in an analytical form,

$$\begin{aligned} \langle \psi_{n'l'm'} | d | \psi_{nlm} \rangle &= \frac{(-1)^{n'-n}}{n^{*'} - n^*} (n^* n^{*'})^{11/6} \left(\frac{n^* + n^{*'}}{2} \right)^{-5/3} \\ &\times [\mathbf{J}_{n^{*'}-n^*-1}(n^{*'} - n^*) + \mathbf{J}_{n^*-n^{*'}+1}(n^{*'} - n^*)] I_{ml}^{m'l'}, \end{aligned} \quad (18)$$

where $\mathbf{J}_\nu(z)$ is the Anger function [8] and $I_{ml}^{m'l'}$, are integrals of spherical harmonics representing the angular part [9]. For example, this semiclassical expression predicts for the dipole moment between the 43s and the 43p state in rubidium a value of $d = 1041$, whereas the exact value is $d = 1069$ [3], i.e., less than 3% discrepancy.

IV. LASER EXCITATION TO RYDBERG STATES

Let us now turn to the question of producing Rydberg atoms in an experiment. The most commonly used way is to excite ground state atoms optically using laser light. This can be done using one-photon processes, where the ground state is directly coupled to the Rydberg state, or via multi-photon schemes using one or two intermediate (non-Rydberg) states. We will first focus on the case of direct excitations. In the case of rubidium, the ground state

has an ionization energy corresponding to a wavelength of $\lambda = 297$ nm, i.e., direct excitation requires UV lasers to access the Rydberg states. These lasers have a frequency resolution that allows to select a single Rydberg state for excitation. Then, we can write the dynamics of the excitation process as a two-level system, involving only the electronic ground state $|g\rangle = |5s\rangle$ and a single Rydberg state $|r\rangle = |np\rangle$. Within the electric dipole approximation, we can treat the laser as an oscillating electric field with peak strength E_0 and couple it to the dipole matrix element d_{gr} of the transition between the ground state and the Rydberg state. Then, we can write the perturbation by the laser field using the Hamiltonian

$$H = \Delta|r\rangle\langle r| + [\Omega \cos(\omega t)|g\rangle\langle r| + \text{h.c.}], \quad (19)$$

where we have introduced the energy difference Δ between the ground state and the Rydberg state and the Rabi frequency $\Omega = d_{gr}E_0$. We now go into the rotating frame of the laser field, i.e., we make the transformation $|r\rangle \rightarrow |r\rangle \exp(i\omega t)$. Inserting this into the Schrödinger equation shifts the $|r\rangle$ level by the frequency ω and leads to the detuning $\delta = \Delta - \omega$. In the rotating-wave approximation, we neglect fast rotating terms on the order of 2ω and obtain the effective Hamiltonian

$$H = \delta|r\rangle\langle r| + \left[\frac{\Omega}{2}|g\rangle\langle r| + \text{h.c.} \right]. \quad (20)$$

When the excitation laser is resonant with the Rydberg transition (i.e., $\delta = 0$), we can diagonalize the Hamiltonian using the two eigenstates

$$|+\rangle = \frac{1}{\sqrt{2}}(|g\rangle + |r\rangle) \quad (21)$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|g\rangle - |r\rangle). \quad (22)$$

In this new basis, the Hamiltonian becomes

$$H = -\frac{\Omega}{2}|-\rangle\langle -| + \frac{\Omega}{2}|+\rangle\langle +|. \quad (23)$$

The system undergoes Rabi oscillation between the ground state and the Rydberg state, i.e., the probability to find the system in the Rydberg state is given by

$$P_r(t) = \cos^2(\Omega t). \quad (24)$$

The value of the Rabi frequency depends on the strength of the laser as the peak field strength E_0 is related to the laser power P , $E_0 \sim \sqrt{P}$. Equally important, however, is the

asymptotic scaling of the Rabi frequency with the principal quantum number. To obtain the relation, we assume that the ground state wave function is essentially a pointlike object compared to the extension of the Rydberg state. Then, we can approximate the ground state wave function by a Dirac delta function at the origin. The corresponding dipole moment is then proportional to the value of the Rydberg wave function at the origin,

$$d_{gr} = \langle 5s | d | np \rangle = \psi_{np}(\mathbf{r} = 0). \quad (25)$$

From the normalization factor of the wave function we obtain $d_{gr} \sim n^{*-3/2}$. This means that the higher the Rydberg state we want to excite, the lower the Rabi frequency will be, i.e., it takes longer to reach the Rydberg state.

As Rydberg states are excited atomic states, they always have a finite lifetime τ , since the coupling to the vacuum of the electromagnetic field provides a natural decay channel. In principle, this decay can happen via two different processes. The first possibility is a sequence of decays through other Rydberg states, by lowering the principal quantum number at most by one during each individual decay event. The second possibility is a direct decay into the ground state (or the lowest electronic state allowed by selection rules) by the emission of a single photon. We will now calculate the scaling behavior with n^* to see which of the two processes is more important.

In both cases, we will use Fermi's golden rule to calculate the decay rate. This is well justified, as the frequency of the emitted photons is always much larger than the corresponding decay rate. According to Fermi's golden rule, the decay rate is given by

$$\gamma = 2\pi |\langle f | V | i \rangle|^2 \rho(\omega), \quad (26)$$

where $|i\rangle$ and $|f\rangle$ are the initial and final state of the decay process, respectively, V is the operator describing the interaction leading to the decay, and $\rho(\omega)$ is the density of states of the environment at its final energy ω [10]. The radiation field has a density of states of $\rho(\omega) = 8\pi\omega^2$, and for electric dipole transitions we have $\langle f | V | i \rangle = \langle f | dE | i \rangle \sim \sqrt{\omega}$. Consequently, we have an overall ω^3 dependence of the decay rate. In the case of decay to adjacent Rydberg levels, the squared dipole matrix element scales as n^{*4} , but this factor is suppressed by a factor of n^{-9} from the ω -dependence. Therefore, the total scaling of the decay rate is $\gamma \sim n^{*-5}$.

In the case a direct decay to the ground state, the frequency of the emitted photon is essentially independent of the principal quantum number n^* . The decay rate is therefore

only determined by the square of the dipole matrix element of the transition, yielding a scaling according to $\gamma \sim n^{*-3}$ for the decay rate. Consequently, the direct decay to the ground state is the most relevant process, resulting in a scaling of $\tau \sim n^3$.

However, there are two exceptions to this scaling behavior. If the Rydberg atoms is brought into a circular Rydberg state with $l = n - 1$, then the only dipole allowed transition is to the adjacent Rydberg state. In this case, the lifetime is only determined by the first process and therefore scales as $\tau \sim n^{*5}$. The other exception arises from finite temperature effects. Instead of being a vacuum, the electromagnetic field is populated with blackbody photons, which can drive transitions between Rydberg states. Then, the lifetime is given by

$$\tau = \frac{3n^{*2}}{4\alpha^3 T}, \quad (27)$$

where α is the fine structure constant and T is the temperature of the environment [11]. Note that while it is possible also to ionize a Rydberg atom by blackbody radiation, this process scales only as $\gamma \sim n^{-7/3}$ and can therefore be neglected compared to blackbody-induced transitions to other Rydberg states [12].

However, it is not always possible to use a single laser to perform Rydberg excitations because of the challenges arising from the relatively short laser wavelength. Therefore, it can be more convenient to use two or three lasers to couple the ground state to the Rydberg state. Because of selection rules, the final Rydberg state will be either a s state or a d state. In rubidium, the laser wavelengths associated with a two-step excitation process are $\lambda_1 = 780$ nm and $\lambda_2 = 480$ nm, respectively. This involves a near-resonant coupling to the intermediate state $|5p\rangle$, which is the first electronically excited state. Since this is not a Rydberg state, the intermediate state will decay very fast with a rate of $\gamma_p = 2\pi \times 6$ MHz, corresponding to a lifetime of only $\tau_p = 26$ ns. We will therefore consider a large detuning Δ from this intermediate state $|p\rangle$, while the energy difference between the ground state $|g\rangle$ and the Rydberg state $|r\rangle$ differing the sum of the two laser frequencies by a two-photon detuning δ . After performing the rotating wave approximation, the Hamiltonian for the three-level system is of the form

$$H = \Delta|p\rangle\langle p| + \delta|r\rangle\langle r| + \frac{\Omega_p}{2}(|g\rangle\langle p| + \text{H.c.}) + \frac{\Omega_c}{2}(|p\rangle\langle r| + \text{H.c.}) = \begin{pmatrix} 0 & 0 & \frac{\Omega_p}{2} \\ 0 & \delta & \frac{\Omega_c}{2} \\ \frac{\Omega_p}{2} & \frac{\Omega_c}{2} & \Delta \end{pmatrix}. \quad (28)$$

As the next step, we will perform an adiabatic elimination of the intermediate state. For this, we expand the wave function $|\psi(t)\rangle$ according to $|\psi(t)\rangle = \psi_g(t)|g\rangle + \psi_r(t)|r\rangle + \psi_p(t)|p\rangle$. The corresponding Schrödinger equation then reads

$$i\dot{\psi}_g = \frac{\Omega_p}{2}\psi_p \quad (29)$$

$$i\dot{\psi}_r = \delta\psi_r + \frac{\Omega_c}{2}\psi_p \quad (30)$$

$$i\dot{\psi}_p = \frac{\Omega_p}{2}\psi_g + \frac{\Omega_c}{2}\psi_r + \Delta\psi_p. \quad (31)$$

We can then eliminate the intermediate state by setting its time derivative to zero, i.e., $\dot{\psi}_p = 0$ [13]. From the solution of the equation of motion for ψ_p we obtain

$$\psi_p = -\frac{\Omega_p}{2\Delta}\psi_g - \frac{\Omega_c}{2\Delta}\psi_r. \quad (32)$$

This expression can only be correct in the limit $\Omega_{p,c} \ll |\Delta|$, i.e., in the limit of large detuning and therefore small population of the intermediate state. We can then insert the expression for ψ_p into the equations of motion for ψ_g and ψ_r , yielding

$$i\dot{\psi}_g = -\frac{\Omega_p^2}{4\Delta}\psi_g - \frac{\Omega_p\Omega_c}{4\Delta}\psi_r \quad (33)$$

$$i\dot{\psi}_r = \left(\delta - \frac{\Omega_c^2}{4\Delta}\right)\psi_r - \frac{\Omega_p\Omega_c}{4\Delta}\psi_g. \quad (34)$$

These equations of motion are exactly equivalent to those generated by an effective Hamiltonian H_{eff} , which is given in the $\{|g\rangle, |r\rangle\}$ basis as

$$H_{\text{eff}} = - \begin{pmatrix} \frac{\Omega_p^2}{4\Delta} & \frac{\Omega_p\Omega_c}{4\Delta} \\ \frac{\Omega_p\Omega_c}{4\Delta} & \frac{\Omega_c^2}{4\Delta} - \delta \end{pmatrix}. \quad (35)$$

Note that the coupling via the intermediate state shifts the resonance condition for the two-photon transition between the ground state and the Rydberg state. It occurs when the two-photon detuning δ cancels the differential AC Stark shift, i.e., $\delta = (\Omega_c^2 - \Omega_p^2)/4\Delta$. On resonance, the system undergoes Rabi oscillations with the effective Rabi frequency $\Omega_{\text{eff}} = \Omega_p\Omega_c/2\Delta$.

Now, we will discuss the optimal choice of the detuning Δ . On the one hand, we want to make Δ very large, as then the unwanted radiative decay from the intermediate state is strongly suppressed. On the other hand, making Δ large also reduces the effective Rabi

frequency, eventually to the point where it becomes smaller than the decay of the Rydberg state. Therefore, we have to find an optimal balance between these two effects. In the following, we assume that the Rabi frequencies for the two transitions are identical, i.e., $\Omega_p = \Omega_c \equiv \Omega$. Then, we find the probability to successfully observe the system without any unwanted decay process (also known as the fidelity f) to be

$$f = (1 - p_p)(1 - p_r), \quad (36)$$

where p_p and p_r are the probability for decay events from the intermediate and from the Rydberg state, respectively. In the limit, where these probabilities are small, we can express them as

$$p_p = |\psi_p|^2 \gamma_p t \approx \frac{\Omega^2}{4\Delta^2} \gamma_p \quad (37)$$

$$p_r \approx \gamma t, \quad (38)$$

where t is the time the system is evolving. Now assume that we want to evolve the system until it has reached a certain fraction ϕ of a Rabi cycle, which requires the time $t = 4\phi\Delta/\Omega^2$. In order to maximize the fidelity f we solve the equation $\partial_\Delta f = 0$, which has the solution

$$\Delta = \pm \sqrt{\frac{\gamma_p}{\gamma}} \frac{\Omega}{2}. \quad (39)$$

Consequently, the optimal choice for the detuning depends on the ratio of the decay rates. It occurs at the point where the errors from the two processes occur with equal probability, i.e., $p_p = p_r$.

Property	Scaling	Rb(5S) - ground state	Rb(43S) - Rydberg state
Binding energy E_{n^*}	$(n^*)^{-2}$	4.18 eV	8.56 meV = 2.07 THz
Level spacing	$(n^*)^{-3}$	2.50 eV (5S-6S)	100.05 GHz (43S-44S)
Orbit radius $\langle r \rangle$	$(n^*)^2$	5.632 a_0	2384.2 a_0
Polarizability α	$(n^*)^7$	-79.4 mHz/(V/cm) ²	-17.7 MHz/(V/cm) ²
Lifetime (spont. decay) τ	$(n^*)^3$	5P _{3/2} -5S _{1/2} : 26.2 ns	42.3 μ s at 300K incl. BBR
transition dip. moment $d_{5P,nS}$	$(n^*)^{-3/2}$	5S _{1/2} -5P _{3/2} : 4.227 ea ₀	5P _{3/2} -43S _{1/2} : 0.0103 ea ₀
transition dip. moment $d_{nP,(n+1)S}$	$(n^*)^{-2}$	—	43P _{3/2} -43S _{1/2} : 1069 ea ₀

TABLE II: Scaling of Rydberg state properties with the principal quantum number n^* and comparison between values for the ground state and 43S.

Finally, Tab. 2 summerizes the scaling properties of Rydberg states, including a comparison between the ground state and the $43s$ state of rubidium [3].

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 - [14] In reality, hydrogen atoms also do not have a permanent electric dipole moment because the interaction with the vacuum of the radiation field results in the Lamb shift that also lifts the degeneracy.