DIPLOMARBEIT

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Chapter 1

Introduction

The two processes, the Fano- and the resonant Auger-process, discussed in this diplomawork are already known for some time and have already been experimentally investigated many times in the spectral domain but time domain experiments are just about to be started. New laser-technologies allowing pulses in the attosecond domain make it possible to resolve the details. The theories for these processes therefore need to be reconsidered and to employ time-dependent approaches. Starting from the time-dependent Schrödinger equation I intend to show the possibilities and occurring problems of a time-dependent theory.

One of the most famous and simple experimental "proofs" of quantum-theory is the "double-slit-experiment" which can not be explained classically. On it's way from its source to the detector the electron doesn't choose one of the slits but passes through both of them at the same time. At the detector contributions form these alternative paths interfere and cause the unexpected distribution. Although the processes studied here are a bit more complicated this basic feature of quantum theory can still be observed in a rather simple way. Of course a proper description of the normal Auger-process also needs to be quantum-theoretically but the very basic principle may be explained to a novice classically. This is not the case here. Although the single steps of the processes are pretty much the same there is no way to explain the obtained spectra without entering the exciting world of qunatum theory. The description of the electrons by wavefunctions that allow to describe the strange behavior mentioned above: The excited electron doesn't choose a single path but propagates in a superposition of them. Just like ordinary waves the wavefunctions that describe these alternative paths interfere and just in the moment of measurement the mixture of wavefunction collapses and fixes the location and energy of the particle causing the asymmetric spectra.

Both processes are two-electron problems. As this makes the mathematical description rather troublesome Ugo Fano developed an alternative procedure, how to convert the Fano-process into an one-particle problems, which might be of general interest. Furthermore this description makes the resonance [3] coming from the exact coincidence of two coupled levels in energy easier to understand.

Throughout this work the square-brackets notation [ ] is used to indicate hole states and atomic units are used, eg $\hbar = 1, e = 1, m_e = 1$. Furthermore a semiclassical approach is used, meaning applying quantum-theory for particles but treating the radiation field classically (not quantized).

Chapter 2

Basic methods

Before the processes are discussed it is important to give a short review of the basic methods that can be used to describe those phenomenons or give reasons why conventional procedures like perturbation theory are not applicable.

Every attempt to study quantum effects will start at the Schrödinger-equation

$$H|\Psi >= i|\dot{\Psi} > \tag{2.1}$$

which unfortunately can analytically only be solved in some few simple cases. Therefore one has to introduce some approximations and simplifications of the real problem or/and make use of numerical technics.

2.1 Interaction representation

In the end every calculation has to provide results that can be compared to experimental results. To derive physically measurable values from the wavefunctions one has to calculate the expectancy value of the corresponding operator: $< A >=< \Psi|A|\Psi >$. From the right side of this equation it can be seen that it is free to choose where (in Ψ or A) to include the time-evolution of the system. In the so called Schrödinger representation A is defined to be constant but the wavefunction $|\Psi >$ is a function of time. The exact opposite of it is called the Heisenbergbild. An intermediate form, where both, Ψ and A, are time-dependent, is the interaction representation which seems at first sight to be needlessly complicated but simplifies things in some cases.

In this approach the hamiltonian H is split into a time-independent unperturbed Hamiltonian H_0 and a time-dependent perturbation V.

$$H(t) = H_0 + V(t) \tag{2.2}$$

Going [4] from the Schrödinger representation to the interaction representation with respect to H_0 is archived by applying the unitarian transformation $T(t) = e^{iH_0(t-t_0)}$ to the vectors and operators A of the Schrödinger representation[1], t_0 being a reference instant that we will take for the origin of time ($t_0 = 0$). This transformation equals the time-evolution operator of a system described by H_0. If $|\tilde{\psi}(t)>$ and $\tilde{A}$ represent the vectors and operators in the new representation, then we have

$$|\tilde{\psi}(t)>= e^{iH_0t}|\psi> \tag{2.3}$$

$$\tilde{A}(t) = e^{iH_0t}Ae^{-iH_0t} \tag{2.4}$$

If V were zero, the interaction representation would be identical to the Heisenberg representation and $|\tilde{\psi}>$ would remain fixed over time. It follows that in the general case, where V is nonzero, $|\tilde{\psi}>$ evolves only as result of the presence of the coupling V. To see this more precisely let us determine the evolution equation of $|\tilde{\psi}>$ by applying $i\frac{d}{dt}$ to (2.3) and by using the Schrödinger equation for the occurring $i\frac{d|\psi(t)>}{dt}$-term. As a result we note

$$\begin{aligned} i\frac{d}{dt}|\tilde{\psi}(t)> &= -H_0|\tilde{\psi}(t)> + e^{iH_0t}(H_0+V)|\psi(t)> \\ &= \tilde{V}|\tilde{\psi}(t)> \end{aligned} \tag{2.5}$$

where $\tilde{V} = e^{iH_0t}Ve^{-iH_0t}$

2.2 Hamiltonian in the field

A good example for such a time-dependent perturbation is a radiation field. The two studied processes are both triggered by an electromagnetic field coming from a laser or a synchrotron.

2.2.1 Minimal-coupling prescription

To derive the proper description for the quantum-mechanical behavior of an electron in a radiation field one has to start from classical electrodynamics and then quantize the electrons motion according to the principles of the first quantization [5]. The classical electrodynamics of an electron in a radiation field can be summarized by the Hamiltonian

$$H = \frac{1}{2m}(\mathbf{p} - \frac{e}{c}\mathbf{A})^2 - e\phi \tag{2.6}$$

[1]To understand operators like H_0 in an exponent one has to expand the exponential function into it's Taylor series.

where $\mathbf{A}$ and ϕ are the vector and scalar potential of the radiation field. This Hamiltonian is justified because it correctly reproduces the equations of motion (Lorenz-force) when substituted into the classical canonical equations:

$$\dot{q}_j = \frac{\partial H}{\partial p_j} \tag{2.7}$$

and

$$\dot{p}_j = -\frac{\partial H}{\partial q_j} \tag{2.8}$$

Using the Hamiltonian from (2.6) in (2.7) leads for the x-component to

$$\dot{x} = \frac{\partial H}{\partial p_x} = \frac{1}{m}(p_x - \frac{e}{c}A_x) \tag{2.9}$$

When it is substituted into (2.8) we get

$$\dot{p}_x = -\frac{\partial H}{\partial q_x} = e\frac{\partial \phi}{\partial x} + \frac{e}{mc}[(p_x - \frac{e}{c}A_x)\frac{\partial A_x}{\partial x} + (p_y - \frac{e}{c}A_y)\frac{\partial A_y}{\partial x} + (p_z - \frac{e}{c}A_z)\frac{\partial A_z}{\partial z}] \tag{2.10}$$

Relationship (2.9) can be used to rewrite (2.10) in the form

$$\dot{p}_x = e\frac{\partial \phi}{\partial x} + \frac{e}{c}(\dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_y}{\partial x} + \dot{z}\frac{\partial A_z}{\partial x}) \tag{2.11}$$

The total time derivative of A_x

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial t} + \dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_x}{\partial y} + \dot{z}\frac{\partial A_x}{\partial z} \tag{2.12}$$

can be used to rewrite (2.11) as

$$\begin{aligned} \frac{d}{dt}(p_x - \frac{e}{c}A_x) &= e(\frac{\partial \phi}{\partial x} - \frac{1}{c}\frac{\partial A_x}{\partial t}) + \frac{e}{c}[\dot{y}(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}) - \dot{z}(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x})] \\ &= e(\frac{\partial \phi}{\partial x} - \frac{1}{c}\frac{\partial A_x}{\partial t}) + \frac{e}{c}[\mathbf{v} \times (\nabla \times \mathbf{A})]_x \end{aligned} \tag{2.13}$$

For all three coordinates this result may be generalized:

$$\begin{aligned} \frac{d}{dt}(\mathbf{p} - \frac{e}{c}\mathbf{A}) &= e(\bigtriangledown\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}) + e[\frac{1}{c}\mathbf{v} \times (\bigtriangledown \times \mathbf{A})] \\ &= e(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B}) \end{aligned} \tag{2.14}$$

For the last conversion we used the Maxwell law $\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} + \bigtriangledown\phi$ and $\mathbf{B} = \bigtriangledown \times \mathbf{A}$. A closer look at (2.14) reveals that the right side of it is the

well known formula for the Lorentz force, what is just what we were ment to show to proof (2.6).

The classical Hamiltonian (2.6) allows us to quantize the electrons motion according to the principles of the first quantization: $\mathbf{p} \rightarrow -i\bigtriangledown$; $r \rightarrow r$ and $H \rightarrow i\frac{\partial}{\partial t}$. We derive the time-dependent Schrödinger equation :

$$\begin{aligned} i\frac{\partial}{\partial t}\Psi(r,t) &= [\frac{1}{2m}(-i\bigtriangledown -\frac{e}{c}\mathbf{A})^2) + V]\Psi(r,t) \\ &= [\mathbf{H}_0 + \mathbf{H}'(t)]\Psi(r,t) \end{aligned} \tag{2.15}$$

This immediately provides the semiclassical electron-field interaction Hamiltonian H':

$$\mathbf{H}'(\mathbf{r},\mathbf{t}) = \frac{e}{2mc}[2i\mathbf{A}\cdot\bigtriangledown + i(\bigtriangledown\cdot\mathbf{A})] + \frac{e^2}{2mc^2}\mathbf{A}\cdot\mathbf{A} \tag{2.16}$$

2.2.2 The gauge invariance and the gauge transformation of the Schrödinger equation

We know that the electromagnetic field strengths are derivable from potentials, which can be gauged in different ways. For example the so-called gauge transformation of the first kind $\mathbf{A'} = \mathbf{A} + \bigtriangledown\chi$ together with $\phi' = \phi + \frac{1}{c}\dot{\chi}$ leaves the field strengths unaltered.
These gauge transformations change the Schrödinger equation (2.15) to:

$$i\frac{\partial\Psi}{\partial t} = [\frac{1}{2m}(-i\bigtriangledown -\frac{e}{c}\mathbf{A'} + \frac{e}{c}\bigtriangledown\chi)^2 - e\phi' + \frac{e}{c}\dot{\chi}]\Psi \tag{2.17}$$

This can be transformed into

$$i\frac{\partial}{\partial t}[e^{i\frac{e}{c}\chi}\psi] = [\frac{1}{2m}(-i\bigtriangledown -\frac{e}{c}\mathbf{A'})^2 - e\phi'][e^{i\frac{e}{c}\chi}\Psi] \tag{2.18}$$

Therefore, the new solution after the gauge transformation is

$$\psi' = e^{i\frac{e}{c}\chi}\psi \tag{2.19}$$

what differs from the old solution by the phase-factor $e^{i\frac{e}{c}\chi}$ only. Whenever we want to calculate any physically measurable value from this ψ', we have to take the expectancy value from it. As this is done by taking the square of it's absolute value such phase-factors cancel out leaving no physical difference between the different gauges of the wavefunction. During the following derivations the "radiation gauge" (also called "Coulomb gauge") will be used:

$$\bigtriangledown\cdot\mathbf{A} = 0 \qquad \varphi = 0 \tag{2.20}$$

2.2.3 The dipole approximation and the two forms of the interaction hamiltonian

In the radiation gauge the Maxwell's equation of the vector potential in the free space ($(\bigtriangledown^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})\mathbf{A} = 0$) can be solved by a monomode constant-amplitude vector potential $A(r,t) = A_0 cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$ where $\mathbf{k}$ is the propagation vector.
The dipole approximation of a radiation field consists of neglecting the "retardation effect" due to the wave vector $\mathbf{k}$ and thus replacing the spatial modulation factor

$$e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1 + \mathbf{k}\cdot\mathbf{r} + \dots \tag{2.21}$$

by the leading term, unity. Since the wavelength in the optical or suboptical region is almost always very large compared to any other characteristic length associated with the atomic system, effectively $|\mathbf{k}\cdot\mathbf{r}| \ll 1$ and hence the dipole approximation turns out nearly always to be very good in practice. With help of (2.20) and (2.21) (2.16) can be transformed into the so-called "velocity gauge"

$$\mathbf{H'(t)} = \frac{ie}{mc}\mathbf{A(t)}\cdot\bigtriangledown + \frac{e^2}{2mc^2}\mathbf{A(t)}^2 \tag{2.22}$$

where $\mathbf{A(t)}$ is (because of (2.21)) independent of the coordinates.
It is now convenient to introduce a transformed interaction Hamiltonian, obtained by making a gauge transformation of the second kind:

$$\psi = e^{i\frac{e}{c}\mathbf{r}\cdot\mathbf{A(t)}}\Psi \tag{2.23}$$

Substituting this expression in (2.15) together with the definition for the electric field strength, namely $\mathbf{E} = -\frac{1}{c}\frac{\partial A(t)}{\partial t}$, yields the interaction Hamiltonian in the "length form"

$$\mathbf{H'(t)} = -e\mathbf{rE}(t) \tag{2.24}$$

2.2.4 Selection rules

In the following chapters the probability of transitions, occurring as a consequence of an external field, will be proportional to the matrix element $< n'l'm'm'_s|\mathbf{r}|nlmm_s >$, where n, l, m, m_s (n', l', m', m'_s) represent the quantum numbers of the initial (final) state. The following selection rules for the dipole-transitions can be derived [6]:

1. $\Delta m_s = 0$
2. $\Delta m = 0, \pm 1$

3. $\Delta j = 0, \pm 1$

4. for $j = 0$ follows $j' \neq 0$

5. $|nlmm_s >$ and $|n'l'm'm'_s >$ need to have different parity. (if spin-orbital coupling is neglected)

2.3 Perturbationtheory and transitionprobability

In the introduction to this chapter it was already mentioned that it will often be impossible to solve the full Schrödinger equation. Sometimes the solutions of an unperturbed system are known but the influence of a small perturbation (e.g:radiation) makes calculation too complicated. In this case it might be convenient to start from the unperturbed solutions and try calculate its changes due to the perturbations. This is done by the perturbation theory.

2.3.1 Time-independent Perturbation theory

This theory may be applied to systems which can be described by a hamiltonian

$$H = H_0 + \lambda V \tag{2.25}$$

that consists of the unperturbed hamiltonian H_0 and the small time-independent perturbation λV. We assume the orthonormal eigenfunctions of the unperturbed problem are known: $H_0|a_0 >= E_{a_0}|a_0 >$. We try to solve the whole problem

$$H|a >= E_a|a > \tag{2.26}$$

by a Taylor-expansion of $|a >$

$$|a >= |a_0 > +\lambda|a1 > +\lambda^2|a_2 > +O(\lambda^3) \tag{2.27}$$

and of E_a

$$E_a = E_{a_0} + \lambda E_{a_1} + \lambda^2 E_{a_2} + 0(\lambda^3) \tag{2.28}$$

Insertion of this ansatz into (2.26) leads us to

$$\begin{aligned}(H_0 + \lambda V)(|a_0 > +\lambda|a1 > +\lambda^2|a_2 > +O(\lambda^3)) = \\ = (E_{a_0} + \lambda E_{a_1} + \lambda^2 E_{a_2} + 0(\lambda^3))(|a_0 > +\lambda|a1 > +\lambda^2|a_2 > +O(\lambda^3))\end{aligned} \tag{2.29}$$

This equation can be solved by coefficient comparison. We will direct our attention to the addends of first order of λ and project $|b_0>$ onto it. This yields for $b = a$ the first order energy correction

$$E_{a_1} =< a_0|V|a_0 > \tag{2.30}$$

For $a \neq b$ we obtain

$$< b_0|a_1 >= \frac{< b_0|V|a_0 >}{E_{a_0} - E_{b_0}} \tag{2.31}$$

Making use of the orthonormality of the unperturbed solutions $< b|a >= \delta_{ab}$ and $< a_0|a_1 >= 0$ enables us to calculate the first order correction of $|a_1 >$

$$|a_1 >= \sum_{b \neq a} |b_0 >< b_0|a_1 > \tag{2.32}$$

A similar derivation [4] for the second order terms of λ results in

$$E_{a_2} = \sum_{c \neq a} \frac{|V_{ca}|^2}{E_{a_0} - E_{c_0}} \tag{2.33}$$

These results make it obvious that we have to deal with severe problems because of the occurring poles when we will analyze resonances in the following chapters.

2.3.2 Time-dependent perturbation theory

The perturbation V(t) introduced by a laser is time-dependent and therefore needs to be treated according to another theory. The system under study is represented by the hamiltonian

$$H = H_0 + V(t) \tag{2.34}$$

Again it is assumed that the orthonormal eigenfunctions of H_0: $H_0|n >= E_{n0}|n >$ are known and the solution $\psi(t)$ is expanded in terms of them.

$$|\psi(t) >= \sum_n |n > c_n(t) e^{-iE_n(t-t_i)} \tag{2.35}$$

The insertion of this ansatz into the Schrödinger equation leads to

$$\sum_n V c_n e^{-iE_n(t-t_i)}|n >= i \sum_n \dot{c}_n e^{-iE_n(t-t_i)}|n > \tag{2.36}$$

Finally we project another orthonormal state $< m|$ onto it and derive an integral equation for c_m

$$c_m(t) = \delta_{mm_0} - i \sum_n \int_{t_1}^{t} dt' < m|V(t')n > c_n(t') e^{-i\omega_{nm}(t'-t_i)} \tag{2.37}$$

where $\omega_{nm} = E_n - E_m$ and the initial value was set to $c_m(t_i) = \delta_{mm_0}$

2.3.3 Perturbative expansion of transition amplitudes

Assume we know the status (wavefunction) of the system for $t = t_i$ and want to calculate from this the further development. This can be done by a time-evolution operator $U(t_f, t_i)$ which has to fulfill the following equation: $|\psi(t_f) >= U(t_f, t_i)|\psi(t_i) >$. It can be shown [7] that U is given by $U = e^{-iH(t_f - t_i)}$. The evolution operator for a perturbated system can be expanded to the integral equation

$$U(t_f, t_i) = U_0(t_f, t_i) - i \int_{t_i}^{t_f} dt\, U_0(t_f, t_i) V U(t_f, t_i) \tag{2.38}$$

where $U_0 = e^{-iH_0(t_f - t_i)}$ is the evolution operator for the unperturbed system. To prove this one has to show that $U(t_i, t_i) = 1$ and that (2.38) satisfies the evolution equation:

$$i\frac{d}{dt}U(t_f, t_i) = (H_0 + V)U(t_f, t_i) \tag{2.39}$$

By successive iterations (2.38) leads to

$$U(t_f, t_i) = U_0(t_f, t_i) + \sum_{n=1}^{\infty} U^{(n)}(t_f, t_i) \tag{2.40}$$

where

$$U^{(n)}(t_f, t_i) = (-i)^n \int d\tau_n \dots d\tau_n d\tau_1 e^{-iH_0(t_f - \tau_n)} V \dots V e^{H_0(\tau_2 - \tau_1)} V e^{-iH_0(t_1 - t_i)} \tag{2.41}$$

This result can be clearly understood: In lowest order the state develops from t_i to t_f according to H_0. In first order approximation we divide the time-interval into two time-slots, during which we still consider H_0-time-development but at the instant in between we consider the perturbation coming from V. In higher order the time-interval is divided more and more often. This principle is depicted in fig: 2.1. In the interaction-representation this result is

$$\tilde{U}(t_f, t_i) = 1 + \sum_{n=1}^{\infty} \tilde{U}^{(n)}(t_f, t_i) \tag{2.42}$$

where

$$\tilde{U}^{(n)}(t_f, t_i) = (-i)^n \int d\tau_n \dots d\tau_n d\tau_1 \tilde{V}(\tau_n) \dots \tilde{V}(\tau_2) \tilde{V}(\tau_1) \tag{2.43}$$

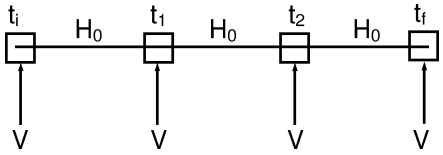

Figure 2.1: Pictorial presentation of the perturbative expansion of transition amplitudes

Let L_{fi} be the matrix element of $\tilde{U}(t_f, t_i)$ between the H_0-eigenstates $< \varphi_f|$ and $|\varphi_i >$

$$L_{fi} =< \varphi_f|\tilde{U}(t_f, t_i)||\varphi_i > \tag{2.44}$$

The perturbative expansion (2.42) thus yields

$$L_{fi} = \delta_{fi} + \sum_{n=1}^{\infty} L_{fi}^{(n)} \tag{2.45}$$

where

$$L_{fi}^{(n)} =< \varphi_f|\tilde{U}^{(n)}(t_f, t_i)|\varphi_i > \tag{2.46}$$

First order transition amplitude

We want to specialize this result on the case of a constant perturbation V during the time-interval $t_i = -T/2 < t < t_f = +T/2$. For n=1 (2.41) yields

$$L_{fi}^{(1)} = -i \int_{t_i}^{tf} d\tau_1 V_{fi} e^{i(E_f - E_i)\tau_1} \tag{2.47}$$

where we have defined $V_{fi} :=< \varphi_f|V|\varphi_i >$. The integration can be executed and we obtain

$$L_{fi}^{(1)} = -2\pi i V_{fi} \delta^{(T)}(E_f - E_i) \tag{2.48}$$

where

$$\begin{aligned} \delta^{(T)}(E_f - E_i) &= \frac{1}{2\pi} \int_{-T/2}^{T/2} d\tau_1 e^{i(E_f - E_i)\tau_1} \\ &= \frac{sin(E_f - E_i)T/2}{\pi(E_f - E_i)} \end{aligned} \tag{2.49}$$

It can be seen that $\delta^{(T)}(E_f - E_i)$ tends to $\delta(E_f - E_i)$ for $T \to \infty$. It's maximal amplitude $T/2\pi$ is obtained for $E_f - E_i = 0$, and it's with is of the order of $4\pi/T$ (distance between the first two zeros on either side of the maximum).

Second order transition amplitude

From a similar derivation [8] the second order transition amplitude can be obtained.

$$L_{fi}{}^2 = -2\pi i \lim_{\eta\to 0_+} \sum_k \frac{V_{fk}Vki}{E_i - E_k + i\eta}\delta^{(T)}(E_i - E_f) \tag{2.50}$$

This formula can be interpreted as a transition in two steps. In a first step the electron is scattered by the perturbation V_{ki} from the initial level i into an intermediate level k and then it is driven from there to the final level, V_{kf}. As there may exist several possible intermediate states we have to take the weighted sum of all of them.

All together the lowest three orders give

$$L_{fi} = \delta_{fi} - 2\pi i\delta^{(T)}(E_i - E_f)[V_{fi} + \lim_{\eta\to 0_+} \sum_k \frac{V_{fk}Vki}{E_i - E_k + i\eta}] \tag{2.51}$$

Transition probability

The probability for a transition from $|\varphi_i>$ to a different state $|\varphi_f>$ due to V is obtained by squaring (2.51)

$$P_{fi}(T) = |L_{fi}|^2 = 4\pi^2[\delta^{(T)}(E_i - E_f)]^2|V_{fi} + \lim_{\eta\to 0_+} \sum_k \frac{V_{fk}Vki}{E_i - E_k + i\eta}|^2 \tag{2.52}$$

If the final state belongs to an energy continuum, $P_{fi}(T)$ is no longer a transition probability, but rather a transition probability density. At the lowest order in V we obtain

$$\delta P(E_f, \beta_f, T) = 4\pi^2 \int_{\substack{E\in\delta E_f \\ \beta\in\delta\beta_f}} dE\, d\beta\, \rho(E,\beta)|v(E,\beta;\varphi)|^2[\delta^{(T)}(E - E_i)]^2 \tag{2.53}$$

where the final states are characterized by their energy E_f and a group of other physical variables designated by β. $v(E,\beta;\varphi)$ is the matrix element $< E,\beta|(T)|\varphi_i >$ which is to be calculated via (2.51). For sufficient large T (large in comparison to the changing of the function $\rho(E,\beta)|v(E,\beta;\varphi)|^2$) we may replace $\delta^{(t)}$ by a delta function centered on E_i. Because the integral over E of $[\delta^{(t)}]^2$ is equal to $T/2\pi$, it is justified to write

$$[\delta^{(t)}(E - E_i)]^2 = \frac{T}{2\pi}\delta^{(t)}(E - E_i) \tag{2.54}$$

Now we are capable to define a transition probability per unit time $\delta w(E_f, \beta_f)$

$$\begin{aligned}\delta w(E_f, \beta_f) &= \frac{1}{T}\delta P(E_f, \beta_f, T) \\ &= 2\pi \int_{\substack{E\in\delta E_f \\ \beta\in\delta\beta_f}} dE\, d\beta\, \rho(E,\beta)|v(E,\beta;\varphi_i)|^2[\delta^{(T)}(E-E_i)]\end{aligned} \tag{2.55}$$

Assuming that the interval δE_f contains E_i and that δE_f is greater than the with 1/T of $[\delta^{(t)}]$, the integration over E is straightforward. As a result we finally note the Fermi golden rule for the transition probability per unit time and per unit interval $\delta\beta$

$$\frac{\delta w(E_f,\beta)}{\delta\beta_f} = 2\pi|v(E_f = E_i, \beta_f;\varphi_i)|^2\rho(E_f = E_i, \beta_f) \tag{2.56}$$

2.4 Nonperturbative calculation of transition amplitudes - the resolvent

With help of the resolvent we will derive a formal, nonperturbative solution of (2.38)

$$U(t,t') = U_0(t,t') - i\int_{t'}^{t} dt_1 U_0(t,t_1)VU(t_1,t') \tag{2.57}$$

The constraint imposed that t_1 varies only between t' and t prevents the integral from being a convolution product. To eliminate this constraint and to obtain a true convolution product that transforms into a simple product by Fourier-transformation, we now introduce four new operators [2].

$$K_+(t,t') = U(t,t')\theta(t-t') \tag{2.58}$$

$$K_{0+}(t,t') = U_0(t,t')\theta(t-t') \tag{2.59}$$

$$K_-(t,t') = -U(t,t')\theta(t'-t) \tag{2.60}$$

$$K_{0-}(t,t') = -U_0(t,t')\theta(t'-t) \tag{2.61}$$

Under consideration of $d\theta(x)/dx = \delta(x)$ we insert this ansatz into (2.39) and we get as result

$$(i\frac{d}{dt} - H)K_+(t,t') = \delta(t-t') \tag{2.62}$$

[2]Heaviside function: $\theta(t-t') = \begin{cases} 1 & t > t' \\ 0 & t < t' \end{cases}$

This is the reason why K_+ is sometimes called "retarded Green's function". Multiplying (2.57) with $\theta(t-t')$ and replacing $\int_{t'}^{t}$ by $\int_{-\infty}^{\infty}\theta(t-t_1)\theta(t_1-t')$ guides us to a true convolution product

$$K_+(t,t') = K_{0+}(t,t') - i\int_{-\infty}^{\infty} dt_1 K_{0+}(t,t_1)VK_+(t_1,t') \tag{2.63}$$

Next we define the Fourier transform of $K_+(t,t')$, which actually depends on $\tau = t-t'$

$$K_+(\tau) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau}G_+(E) \tag{2.64}$$

and it's inversion

$$G_+(E) = -i\int_{-\infty}^{\infty} d\tau\, e^{iE\tau}K_+(\tau) \tag{2.65}$$

Since $K_+(\tau) = e^{-iH\tau}\theta(\tau)$ we can rewrite this as

$$\begin{aligned} G_+(E) &= -i\int_0^{\infty} d\tau\, e^{i(E-H)\tau} \\ &= \lim_{\eta\to 0_+} -i\int_0^{\infty} d\tau\, e^{i(E-H+i\eta)\tau} \\ &= \lim_{\eta\to 0_+}\frac{1}{E-H+i\eta} \end{aligned} \tag{2.66}$$

It is easily verified that

$$G_-(E) = \lim_{\eta\to 0_+}\frac{1}{E-H-i\eta} \tag{2.67}$$

The function $G_+(E)$ ($G_-(E)$) is often refereed to as retarded (advanced) propagator. Now we can fourier transform (2.64)

$$G_+(E) = G_{0+}(E) + G_{0+}VG_+(E) \tag{2.68}$$

where G_{0+} is the retarded propagator associated with H_0. In a next step we introduce the resolvent

$$G(z) := \frac{1}{z-H} \tag{2.69}$$

as a function of the complex variable z. It is connected to $G_\pm$ by

$$G_\pm(E) = \lim_{\eta\to 0_+} G(E\pm i\eta) \tag{2.70}$$

Furthermore we remember that from $G_\pm$ we can calculate $K_\pm$ via the contour integral (2.64). Thinking of their definitions we realize that

$$U(\tau) = K_+(\tau) - K_-(\tau) \tag{2.71}$$

From this we can derive

$$\begin{aligned} U(\tau) =& \frac{1}{2\pi i}\int_{-\infty}^{\infty} dE e^{-iE\tau}[G_-(E) - G_+(E)] \\ =& \frac{1}{2\pi i}\int_{C_+ + C_-} dz e^{-iz\tau} G_(z) \end{aligned} \tag{2.72}$$

where C_+ (C_-) is the contour immediately above (below) the real axis followed from right to left (v.v.)

From this result it is obvious that G(z) contains all the information from H. In many cases it is more convenient to use the resolvent instead of the hamiltonian. G(z) is analytic in C aside from the real axis. The singularities, which are all on the real axis, consist of poles located at discrete eigenvalues of H and of cuts [3] extending over the intervals corresponding to the continuous spectrum of H [9].

2.5 Rabi-frequency

Before going to more complicated processes we want to examine the simplest suggestive model for an atom-laser interaction. The atom is reduced to a two level-atom (orthonormal eigenfunctions $|g>$ and $|e>$ of H_0, corresponding energies ε_g and ε_e) and the laser field is assumed to be monochromatic (ω; dipole approximation). In this approximation the Schrödinger equation for an atom exposed to a radiation field is:

$$H = H_0 + \mathbf{r}\cdot\mathbf{E} = H_0 + zE_0\cos\omega t \tag{2.73}$$

We build an ansatz for the solution from the unperturbed eigenstates

$$\psi = c_g(t)|g> + c_e(t)|e> \tag{2.74}$$

This is substituted into (2.73) and $< g|$ or $< e|$ is projected onto it.

$$\dot{c}_g = -i\varepsilon_g c_g + i\Omega_R\cos(\omega t)c_e \tag{2.75}$$

$$\dot{c}_e = -i\varepsilon_e c_e + i\Omega_R\cos(\omega t)c_g \tag{2.76}$$

[3] A cut is characterized by the fact that the matrix elements of G(z) do not tend to the same value when z tends from below or above towards a point on the real axis located on the cut. A so-called Riemann sheet is a extension of G(z) coming from the upper half-plane toward the lower half plane. The complex poles of this new (not necessarily analytic) function describe unstable states of the system (complex energy leading to exponential damping

where we have introduced the "Rabi flopping frequency" Ω_R for the matrix element.

$$\Omega_R = E_0| < g|z|e > | \tag{2.77}$$

For further calculations it is convenient to transform (2.75) and (2.76) into the interaction representation

$$\dot{c}_g = i\Omega_R \cos(\omega t) e^{i(\varepsilon_g - \varepsilon_e)t} c_e \tag{2.78}$$

$$\dot{c}_e = i\Omega_R \cos(\omega t) e^{-i(\varepsilon_g - \varepsilon_e)t} c_g \tag{2.79}$$

Expanding $\cos(\omega t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$ and applying the rotating wave approximation (which means neglecting higher frequencies) guides us to

$$\dot{c}_g = i\frac{\Omega_R}{2} e^{i\Delta\omega t} c_e \tag{2.80}$$

$$\dot{c}_e = i\frac{\Omega_R}{2} e^{-i\Delta\omega t} c_e \tag{2.81}$$

where $\Delta\omega = \omega - (\varepsilon_e - \varepsilon_g)$. To solve this system of coupled differential equations we substitute:

$$c_e(t) = \tilde{c}_e(t) e^{-i\Delta\omega t/2} \tag{2.82}$$

$$c_g(t) = \tilde{c}_g(t) e^{i\Delta\omega t/2} \tag{2.83}$$

The system now can be rewritten as

$$i \cdot \begin{pmatrix} \dot{\tilde{c}}_g \\ \dot{\tilde{c}}_e \end{pmatrix} = \begin{pmatrix} \Delta\omega/2 & -\Omega_R/2 \\ -\Omega_R/2 & -\Delta\omega/2 \end{pmatrix} \cdot \begin{pmatrix} \tilde{c}_g \\ \tilde{c}_e \end{pmatrix} \tag{2.84}$$

The matrixes eigenvalues are:

$$\Omega = \pm\sqrt{\Omega_R^2 + \Delta\omega^2} \tag{2.85}$$

We assume that the electron is in the excited state at t=0. The initial condition corresponding to this assumption is $c_e(t) = 1$ and $c_g(0) = 0$: The

solutions for this problem is[4]

$$c_g(t) = e^{+i\Delta\omega t/2}\frac{\Omega_R}{\sqrt{\Omega_R^2+\Delta\omega^2}}\sin(\frac{\Omega}{2}t) \tag{2.86}$$

As usual we are interested in the expectancy value:

$$|c_g(t)|^2 = \frac{\Omega_R^2}{\Omega_R^2+\Delta\omega^2}\sin^2(\frac{\Omega}{2}t) \tag{2.87}$$

The probability for the electron to be found in the excited state can be calculated from

$$\begin{aligned} |c_e(t)|^2 =& 1-|c_g(t)|^2 \\ =& 1-\frac{\Omega_R^2}{\Omega_R^2+\Delta\omega^2}+\frac{\Omega_R^2}{\Omega_R^2+\Delta\omega^2}\cos^2(\frac{\Omega}{2}t) \end{aligned} \tag{2.88}$$

From this formula it can be seen that

- the probability oscillates between the two states with the frequency $\frac{\Omega}{2}$
- for $\Delta\omega = 0$ the amplitude of the sinus equals 1 and therefore the electron totally leaves the upper (=initial) state and can at a certain instant be certainly found in the lower state.
- for $\Delta\omega \neq 0$ the frequency of the oscillation is increased and the amplitude decreased according to a lorenz curve. The occupation-probability of the excited state always remains unequal zero.

2.6 Dressed states and stark shift

The atomic dynamics can alternatively be described in terms of a dressed state basis instead of bare states $|e>$ and $|g>$. The dressed states $|1>$ and

[4]How to solve homogen systems of N linear differential equations of first order:

1. Bring the system into the matrix form: $\mathbf{y'} = \mathbf{My}$
2. Calculate the eigenvalues of the matrix M: r_i
3. To each simple root belongs a system of particular solutions $y_1 = A_1e^{r_ix}, y_2 = A_2e^{r_ix}, \ldots, y_N = A_Ne^{r_ix}$
4. The coefficient vector $\mathbf{A}$ can be derived from $(\mathbf{M}-r_i\mathbf{E})\mathbf{A} = 0$ where the coefficient vector $\mathbf{A}$ can be calculated up to an arbitrary constant. If all roots of the characteristic equation are different, the sum of all these particular solutions contains N independent constants, so that we always obtain the general solution.

$|2>$ are eigenstates of the Hamiltonian and, by convention, the state $|1>$ is the one with the greatest energy. They are conveniently expressed in terms of the bare states via the Stückelberg angle $\theta/2$ as

$$|1>= sin\theta|g> +cos\theta|e> \tag{2.89}$$

$$|2>= cos\theta|g> -sin\theta|e> \tag{2.90}$$

where $sin(2\theta) = -\Omega_R/\Omega$, $cos(2\theta) = \Delta/\Omega$, where we have set $\Omega = ({\Omega_R}^2 + \Delta^2)^{\frac{1}{2}}$. The corresponding eigen-energies are $E_1 = \frac{1}{2}\Omega$, $E_2 = -\frac{1}{2}\Omega$. These energies are illustrated in Fig 2.2 [8] as a function of the detuning Δ. The dressed levels repel each other and form an anticrossing at resonance $\omega = \omega_0$. As the detuning Δ varies from positive to negative values, state $|1>$ passes continuously from the excited state $|e>$ to the bare ground state $|g>$, with both bare states having equal weights at resonance. The distances between the perturbed states and their asymptotes for $|\Delta| \gg \Omega_R$ represent the ac Stark shifts, or light shifts, of the atomic states coupled to the laser. The ac-stark-shift of $|g>$ is positive for $\Delta < 0$ and negative for $\Delta > 0$. (vice versa for $|e>$.)

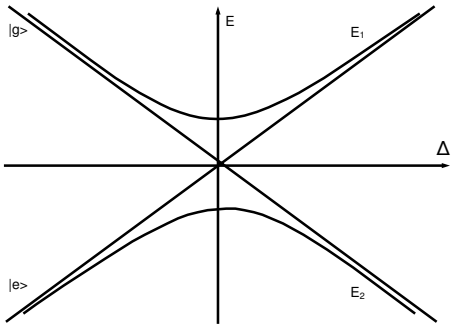

Figure 2.2: Dressed levels of a two-level atom driven by a classical monochromatic field as a function of the detuning Δ

2.7 Pump-probe principle

In order to experimentally study the time dependency inner shell processes a so called "pump-probe"approach is employed. It is made use of the effect that a strong light field affects the electron's motion and can be used to probe the emission [10]. A first sufficiently short XUV-pulse excites the probe and triggers the process under examination. In the following the ejected electron is accelerated in the laser field of the probing-pulse. The electrons final velocity depends on the instant of it's ionization: t_i.
In a simple classical model we derive for a laser field E

$$F = m * a = m * \frac{\partial v}{\partial t} = eE \Rightarrow \frac{\partial v}{\partial t} = \frac{e}{m}E \tag{2.91}$$

leading to

$$v(t) = -\frac{e}{m}A(t) + [v_0 + \frac{e}{m}A(t_i)] \tag{2.92}$$

where v_0 is the electrons initial velocity. This velocity distribution can for example be measured by a "time-of-flight" spectroscope.

The amplitude of populating a state $|v>$ with kinetic momentum v at the moment T after the end of both the laser and the x-ray pulses can also be calculated quantum mechanically [11]. The electron undergoes transitions from the ground state $|0>$ to continuum states which we label by the kinetic momentum of the outgoing electron $|v>$. As it is accelerated in the field, it immediately acquires a high velocity, so that the role of the remaining ions potential V(x) can be neglected. The time-dependent wavefunction can be expanded as [12]

$$|\Psi(t)>= e^{iI_p t}a(t)|0> + \int dv\, b(v,t)|v>) \tag{2.93}$$

where $a(t) \approx 1$ is the groundstate amplitude, and b(v,t)are the amplitudes of the corresponding continuum states. We have factored out the free oscillations of the ground-state amplitude with the bare frequency I_p. Under certain assumptions [13] the Schrödinger equation for b(v,t) reads as

$$\dot{b}(v,t) = -i(\frac{v^2}{2} + I_p)b(v,t) - Ecos(t)\frac{\partial b(v,t)}{\partial v_x} + iEcos(t)d(v). \tag{2.94}$$

Here $d(v) =< v|x|0 >$ denoted the atomic dipole element for bound free transitions. This equation (2.94) can be solved and b(v,t) can be written in the closed form

$$b(v,t) = i\int_0^t dt' Ecos(t')d_x(v+A(t)-A(t'))e^{-i\int_{t'}^t dt''[(v+A(t)+A(t'')^2/2+I_p]} \tag{2.95}$$

Chapter 3

Resonant auger process

3.1 Introduction

3.1.1 Nomenclature

Before explaining the process it is convenient to define the occurring states, energies etc.

- H is the neutral hamiltonian with the corresponding energy E
- H^+ is the Hamiltonian of the singly ionized state with the corresponding energy E^+
- H^{++} is the Hamiltonian of the doubly ionized state with the corresponding energy E^{++}
- H_γ the photon-electron interaction operator
- D is the dipole-operator
- $|g>$ is the ground state with the energy E_g, eigenstates of H
- $|n>$ is a complete set of orthonormal Rydberg levels of H^+ with energy E_n. They are labelled by their principal quantum number n.
- $|\tau>$ is the intermediate state of the excited electron before the shake process takes place; Its energy is τ, which is negative if it is bound. Eigenstate of H^+. Sometimes it is replaced by $|[i]\tau>$ to stress the inner shell hole $[i]$ ($E_{[i]\tau}$)
- $|n'>$ is a complete set of orthonormal Rydberg levels of H^{++} with energy E'_n. They are labelled by their principal quantum number n'

- $|\tau' >$ is the final state of the excited electron after the shake process with energy τ'. Eigenstate of H^{++}
- $|\varepsilon_A >$ is the auger electron at energy ε_A
- $|\varepsilon_A^0 >= E^+ - E^{++}$ is the nominal auger electron energy
- $|\varepsilon >$ is the excited (bound or free) former inner shell electron at energy ε
- $|a >$ and $|b >$ are two states that are coupled by coulomb interaction. In presence of an inner-shell hole they undergo an auger decay
- $|f >$ is the final state at energy E_F which is for example $E_F = E_g + I_F + \varepsilon$ in the resonant case
- ω incident radiation energy
- $E_{exc} = \varepsilon + \varepsilon_a - \varepsilon_a^0$
- $\Gamma_{[i]}$ is the total width of the life-time broadened intermediate hole state [i]

Sometimes states of the whole atom will be labelled by their differences to the neutral atom. eg: $|[f, f']\tau >$ represents the atomic state with two holes and the ε-electron in state $|\tau' >$

3.1.2 A short introduction to the normal Auger effect

The normal Auger effect has been discovered experimentally by P. Auger in 1925 and was explained two years later by Wentzel.

The Auger-process can be modelled as a two step process [14]: At first an incident radiation ω causes an inner-shell electron to leave the atom which therefore remains with an inner-shell hole. This so called Auger (or autoionizing) state can be seen as an excited, quasi-discrete state of a system which is embedded in the continuum of the next higher charge state of the system. This one-particle representation will be explained in more detail in section 3.13. In the following an electron $|a >$ drops down to fill the inner-shell hole and passes the gained energy in a non-radiative process via Coulomb-interaction to another electron in state $|b >$ which then leaves the atom as the Auger electron $|\varepsilon_A >$.

Once it is excited the decay-probability can be calculated according to Fermis golden rule:

$$P_{i\to f} \propto | < f| \sum \frac{e^2}{r_{if}} |[i]\varepsilon > |\delta(E_{[i]\varepsilon} - E_f - \varepsilon_A)\rho(\varepsilon_A) \tag{3.1}$$

where the $\rho(\varepsilon_A)$ is the density of Auger-states in the continuum. This Auger-electron causes a symmetric peak following a Lorenzian in the double differential cross section of ejected electrons (fig 3.1).

In it's final state the atom is therefore doubly ionized. The process can be summarized as following:

$$\omega + A \to A^+ + |\varepsilon > \to A^{++} + |\varepsilon > + |\varepsilon_a > \tag{3.2}$$

and be depicted as presented in figure 3.2. The transition probability to a state with photoelectron-energy ε and Auger-electron-energy ε_a is [15]

$$T(\varepsilon, \varepsilon_a) = \underbrace{< f|H_\gamma|g >}_{direct} + \sum_{[i]} \int_\varepsilon \frac{\overbrace{< f|H - E|[i]\varepsilon >}^{Auger} \overbrace{< [i]\varepsilon|H_\gamma|g >}^{excitation}}{E - E_{[i]\varepsilon}} \tag{3.3}$$

The direct path is usually omitted as it describes the double photo-ionization which vanishes in the independent-electron approximation [16]. If furthermore the energies $E_{[i]}$ are well separated it is sufficient to consider the summation over one manifold $|[i]\varepsilon >$ at the time. In this case $E_{[i]\varepsilon}$ can be approximated by [15]

$$E_{[i]\varepsilon} \approx E_{[i]} + \varepsilon + \Delta_{[i]} - \frac{i}{2}\Gamma_{[i]} \tag{3.4}$$

Where the level shift $\Delta_{[i]}$ and the width $\Gamma_{[i]}$ are due to the lifetime-broadening. From energy-conservation we derive $E = \omega + E_g = E^+_{[i]} + E_{exc}$ what allows us to rewrite the transitionamplitude

$$T(\varepsilon, \varepsilon_a) \approx \int \frac{< f|H - E|\varepsilon >< \varepsilon|H_\gamma|g >}{E_{exc} - \varepsilon + i\Gamma/2} \tag{3.5}$$

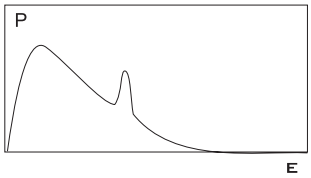

Figure 3.1: Auger-crossection, characteristic Auger-peak on a background of scattered (photo-)electrons.

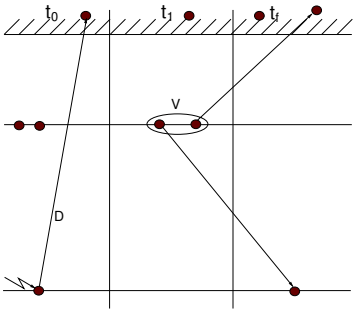

Figure 3.2: The normal Auger process

Alternatively the energy, gained when the electron drops down, could also be lost by emission of radiation. If we want to decide whether for a certain atom we have to expect an Auger or a radiative decay we have to calculate the corresponding Z-dependency of the transition-probability. (Z is the atomic number) According to Fermi's golden rule (2.56) the transitionamplitude for radiative decay is proportional to $\omega^3| < f|z|i > |^2$ (the ω^3 comes from the density of final states of the photonfield). In the hydrogen-approximation ω is proportional to Z and the dipole-matrix-element to $\frac{1}{Z}$ [17]. Therefore the radiative transitionprobability is proportional to $P_{rad} \propto Z^4$. In the same hydrogenic limit the probability for Auger transitions is independent of Z. So we come to the conclusion that for atoms with lower atomic number the Auger decay dominates unless it is forbidden by the selection rules for Coulomb interaction ($\Delta L = \Delta S = \Delta J = 0$; no parity change)

3.1.3 Introduction to the resonant Auger effect

The resonant Auger effect was first experimentally identified at Stanford by Brown in 1980. For the explanation of this effect exist mainly two different approaches: A one-step scattering approach [18] and a more eidetic two-step model [19], which we will make use of. Thus we will treat the process of the x-ray absorbtion and excitation as an event separated in time from the consecutive and incoherent process of deexctitation.

A resonant Auger effect occurs in the case of excitation of an inner-shell electron from $|g >$ to $|\tau >$ which is either a sum of Rydberglevels $|n >$ (Raman region; The levels near threshold are rather dense as with increasing principal quantum number n the states become increasingly dense) or the continuum just above threshold. One has to distinguish between the two following cases: The first one is the so called "participator-decay" where the excited electron takes part in the Auger-decay leading to a final state similar to direct photoemission (this case will be discussed in detail as the Fano-

process in chapter **??**). The decay mechanism now under study is called a spectator-decay, which is depicted in fig 3.3. The excited electron remains in the first instant in it's original state while the Auger decay takes place between two other lower lying electrons $|a>$ and $|b>$. The Auger-electron initially screens the ionic Coulomb field seen by the spectator (or receding photo-) electron. This screening subsides when the (usually fast) Auger-electron passes the bound spectator (slow photoelectron). Distortion of the Auger line shape results and the Auger energy ε_A is raised at the expense of the spectator- (photo-) electron energy ε, what might even lead to recapture of the photoelectron. The whole process can be depicted as:

$$\omega + A \rightarrow |[i]\tau > \rightarrow A^+([f, f']\tau') + \varepsilon_A \tag{3.6}$$

In lowest order approximation and neglecting the direct path the amplitude becomes [15]:

$$A = \sum_{[i]} \sum_{\tau} \frac{< [f, f']\tau' | H - E_F | [i]\tau >< [i]\tau | D | g >}{E_F - E_{[i]\tau} + i\Gamma_{[i]}/2} \tag{3.7}$$

In case of excitation to above threshold the $\sum_\tau$ needs to be replaced by $\int d\tau$. The probability of observing an ejected electron with kinetic energy within the range $(\epsilon, \epsilon + d\epsilon)$ can be formally written by squaring the amplitude and multiplying by a factor $\delta(\epsilon + I_F - \omega)$ which expresses energy conservation. This is valid if it is assumed that the final state $A^+([f, f']\Phi)$ is a stationary state [20]. In principle it will de-excite by cascade Auger and photoemission according to a lifetime Γ_F [20]. This finite lifetime is considered by replacing the delta function by a Lorenzian

$$\frac{dP_F}{d\epsilon} \propto |A_F(\omega, \epsilon)|^2 \frac{1}{(\epsilon - \omega + I_F)^2 + \Gamma^2{}_F/4} \tag{3.8}$$

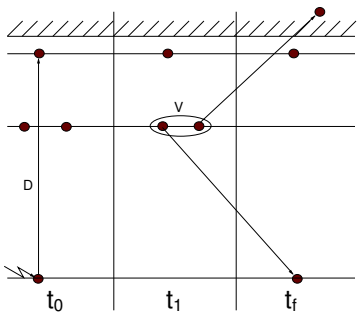

Figure 3.3: The resonant Auger process

3.1.4 Validity of the two-step picture

It may happen that the distribution of intermediate states is sparse so that the spacing between the resonances which contribute to the RA-process is large compared with the intermediate-state width. Therefore the resonances can be considered as non interfering and the two-step approach is justified. If this is not granted one has to consider the phases of the overlapping contributions and calculate the whole process at once.
!!!!!!!!!!!!!!!!!!!!!!!!!!!!
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3.1.5 Changes of the measured Auger electron spectra

Seen from the Auger electrons point of view the difference to the normal Auger decay lies in the additional coulomb interaction to the spectator electron and the resulting changed screening potential it feels as it overtakes the spectator electron. This leads to a shift toward higher kinetic energies relative to the normal Auger spectra [21].

3.2 Influence of the escaping Auger electron on the spectator electron - the shake process

In this first model we will apply the sudden-approximation. This means that we assume that the Auger electron leaves the core immediately and is from the very first moment on out of reach for any further Coulomb interaction. In the instant of the Auger-decay the spectator electron suddenly feels the increased field of a doubly-ionized ion instead of a singly ionized one $H^+ \rightarrow H^{++}$. The spectator electron now is in no eigenstate of the new hamiltonian and therefore will decay into a superposition of the new eigenstates. This process is the so called shake process. (see: fig 3.4) It is often assumed that in (3.7) we can replace

$$< [f, f']\tau'\varepsilon|H - E_F|[i]\tau > \approx \underbrace{< [f, f']\varepsilon|H - E_F|[i] >}_{Augerdecay} \underbrace{< \tau'|\tau >}_{shake} \qquad (3.9)$$

This factorization is assumed to be valid for loosely bound orbitals $< \tau|$ but may fail badly for situations in which it interacts strongly with the ionic

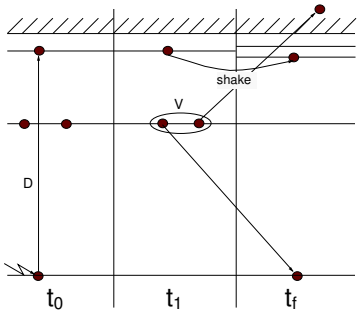


Figure 3.4: The shake process

core. For the moment we assume the state $|\tau>$ consist of a single Rydberg-state $|n>$. According to the selection rules for this transition [16], there is a change only in the principal quantum number and all other should retain their original values. If l=l'and j=j' but $n > n'$ we have shake up or if it is ejected to the continuum shake off. If $n < n'$ we have shake down and for $n = n'$ we have pure spectator transition. Of course $n' = n$ doesn't mean that the state doesn't get modified. It describes the decay from the eigenstate with the principal quantum number n of the old, single-ionized hamiltonian to the eigenstate with n' of the new, double-ionized hamiltonian. The difference between those two states is given by the rather small change of the potential and they will therefore not differ too much.

In case of the first electron being excited just above threshold it is likely it has not moved away too far and the faster Auger electron overtakes it leading to a modified, stronger core-attraction what causes shake down to a bound high-lying level. This special case is often referred to as post-collision interaction (PCI) and will be treated in greater detail in section 3.10.

The so called shake probability $< P_{nn'} = | < n|n' > |^2$ shows some general trends [22]:

- The probability of a pure spectator process n=n' oscillates as a function of n
- Shakeup dominates over shakedown and shakeoff. This can be understood intuitively: The new eigenstates are stronger bound and therefore have for the same value of n lower energies. As the energy of the electron is almost conserved during the shake process shake up is necessary for energy conservation.
- As n' increases the maximum of the shakeup distribution shifts from n=n'+1 toward higher values of n. (the higher n' is, the closer are the levels.

Of course this sudden approximation is not very realistic . In reality the finite time it takes the Auger electron to escape has some influence on the remaining state and on the energy distribution of the Auger electrons.

3.3 Interaction of alternative paths

Assume the spectral with of the laser to be broad enough to excite the inner-shell electron from $|g>$ to two different possible states $|n_1>$ and $|n_2>$. In the following decay to the new, similar eigenstates $|n_1'>$ and $|n_2'>$ there will be a nonzero probability for pure spectator decay $|n_1> \rightarrow |n_1'>$ (and $|n_2> \rightarrow |n_2'>$) but also a non-vanishing shake probability: $|n_1> \rightarrow |n_2'>$ (and $|n_2> \Leftrightarrow n_1'$). Consequently there are two alternative paths from $|g>$ to $|n_1'>$. A good example for this is seen in the resonant Auger spectrum of krypton [23] ($3d_{3/2}^{-1}5p \rightarrow 4p^{-2}n'p$ and $3d_{5/2}^{-1}6p \rightarrow 4p^{-2}n'p$) where the core-excited states are energetically close to each other but at the same time well separated from the other Rydberg states. In general near threshold are many indistinguishable routes to arrive at a given final state leading to interference what results in measuring an asymmetry in the differential cross-section. The experimental results of krypton from [23] are plotted in figure 3.6

The situation gets even more complicated if the life-time broadened intermediate levels overlap. As the energy spacing of adjacent levels becomes less than Γ, that is $E_{exc} \gtrsim -\frac{1}{2}\Gamma^{2/3}$, more and more states contribute to the formation of the intermediate state. Then the calculation of this state is the coherent sum of amplitudes for all possible states $|\tau>= \int \frac{|n><n|D|g>}{E_{exc}-E_n+i\Gamma/2}$. This new phenomenon can be directly derived from (3.7). Squaring the sum leads to mix-term ("$(a+b)^2 = a^2 + \underline{2ab} + b^2$"). The importance of these terms depends on the width of the overlap of the Lorenzian-curves, that belong to each resonance. This overlap is on the one hand fixed by the spectral distance between the resonances but also by the width of the Lorenzian, which

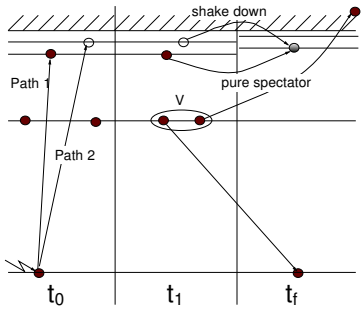


Figure 3.5: Interference between two alternative paths to the same final state

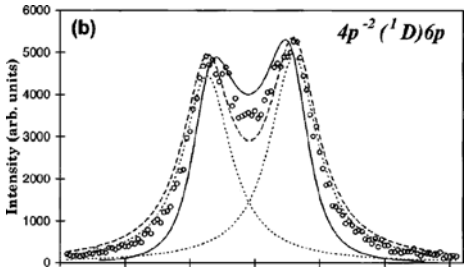


Figure 3.6: Constant final state spectra of the $4p^{-2}(^1D)5p$ group over the photon energy range of the $3d_{372}^{-1}5p$ and $3d_{372}^{-1}6p$ excitations. Dashed lines: fit by two Lorenzian curves; solid lines: fit including interchannel-interference. Taken from [23].

is given by the Auger-decay constant Γ.

3.4 Auger resonant raman effect (ARRE)

There is another speciality of the resonant Auger processes. As in the normal Auger-process the photoelectron is excited to a continuum it's energy-distribution reflects the spectral distribution of the incoming laserpulse and the Auger electron-energy distribution is defined only by the Auger-decay-constant. In the resonant Auger process (sub-threshold-region) the core-electron can only be excited if the incoming photon energy is close to one of the discrete bound energy-levels.

In general every atomic state, that is unstable against further decay with a lifetime ζ, has an uncertainty in it's binding-energies $\Gamma = 1/\zeta$ (Heisenberg's uncertainty relation). This leads to a broadening of the initially discrete resonance at E_r to a permitted energy band $G_r(E - E_r)$. eg: Auger.decay: exponential decay leads to a Lorenzian spectral form of the possible energy values $L_r(E - E_r)$.

Now we want to consider the case of an incoming radiation with a very narrow bandwidth which can for example be taken from a synchrotron. The occurring line-shape distortions of the Auger electron can be described on the basis of energy conservation principle. Initially the system consists of an incoming photon with the energy ω and a target-atom in the ground state. In the end we obtain an atom with two holes and an excited electron with the energy ε and an Auger-electron with the kinetic energy ε_A. Energy-conservation guides to

$$\varepsilon_A = \omega - \varepsilon \tag{3.10}$$

The role of the intermediate excited state is that it selects the suitable photon energies. Let's assume this level is Auger-decay-lorenz-broadened around $E_r \rightarrow L(E - E_r, \Gamma)$. The incoming radiation is distributed according to $\Omega(\omega)$. Thus the relative intensity $I(\varepsilon_A)$ of the resonant Auger electrons is given by

$$I(\varepsilon_A) = \Omega(\omega) * L(E - E_r, \Gamma) \tag{3.11}$$

The product of these two curves is only symmetric if $\Omega(\omega)$ is also symmetric with reference to E_r. Otherwise we obtain an asymmetric spectra

The most outstanding consequence of this so called Auger resonant raman effect (ARRE) is that if a resonant state is excited by a very narrow photon band, then the linewidth of the Auger electron spectrum can be much narrower than the lifetime width of the core excited resonance state [25]. This enables us to do high resolution Auger spectroscopy: e.g. study the finest details of electron correlation

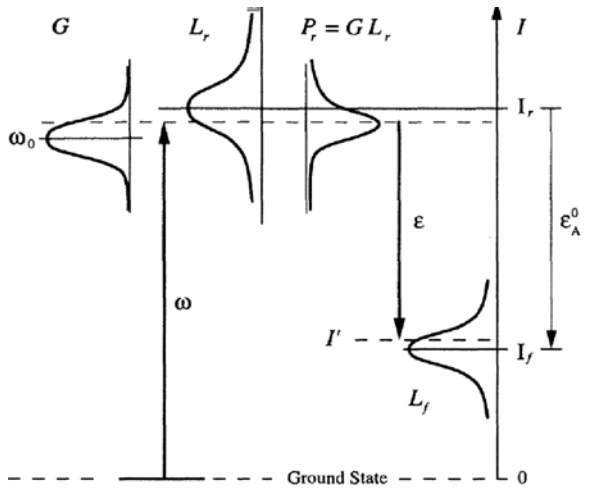


Figure 3.7: Representation of radiationless resonant Raman scattering. An incoming beam of photons with the spectral with G selectively excites intermediate states near the resonant energy I_r, resulting in a intermediate-state population P. Subsequent spectator Auger decay to the final state results in the ejection of electrons with energy ε, determined by the difference in intermediate and final ionic state energies. Taken from [24].

3.5 The "exact" problem

Summarizing the preceding sections we know that three different coupled electrons are involved in this process. Therefore a correct theory would have to be a one step model including three-electron-wavefunctions.

1. The electron being excited and then shaken. It could be represented by

$$|1>= c_{g1}(t)|g> + \sum_n c_n(t)|n> e^{-iE_n t} + \int dE_n c_n(t) e^{-iE_n t}|n> + \\ + \sum_{n'} c_{n'}(t)|n'(r)> e^{-iE_{n'} t} + \int dE_{n'} c_{n'}(t) e^{-iE_{n'} t}|\bar{n'}> \tag{3.12}$$

2. The Auger-electron

$$|2>= c_a(t) e^{-iE_a t}|a> + \int dk c_k(t)|k> e^{-iE_k t} \tag{3.13}$$

3. The dropping electron

$$|3>= c_b e^{-iE_b t}|b> + c_{g2} e^{-iE_g t}|g> \tag{3.14}$$

The antisymetrized product of those single-electron states must fulfill the hamiltonian

$$H = H_0 + D + V_{12} + V_{23} \tag{3.15}$$

As this problem is to complicated we split it into several steps which can be solved under some approximations. (see section 3.1.4)

3.6 Excitation

The first part of the process is the excitation of the inner-shell electron to the intermediate state $|\tau>$. In section 2.5 the behavior of the two-level-atom was already studied. Unfortunately this can not to be generalized to several levels that easily.

We now calculate the population of states due to the excitation from the groundstate by radiation.We make an ansatz:

$$\Upsilon(t) = c_g(t)e^{-i\omega_g t}|g> + \sum c_n(t)e^{-i\omega_n t}|n> \tag{3.16}$$

Inserting this into the Schrödinger equation leads to

$$\dot{c_g}(t) = -i\sum_n c_n(t)E(t)cos(\omega t) < g|z|n > e^{-i(\omega_n - \omega_g)t} \tag{3.17}$$

$$\dot{c_n}(t) = -ic_g(t)E(t)cos(\omega t) < n|z|g > e^{i(\omega_n - \omega_g)t} \tag{3.18}$$

Before excitation the atom is in the groundstate ($c_g(0) = 1$, $c_n(0) = 0$) and the laser doesn't cause much variation of the groundstate amplitude: $c_g(t) \approx 1$. We neglect all dipole-matrix elements but $< g|z|n >$. Thus (3.18) may be rewritten

$$i\dot{c_n}(t) = E(t)e^{-i(\omega_g - \omega_n)t} < n|z|g > \tag{3.19}$$

Formal integration leads to

$$c_n(t) = -i < n|z|g > \int_0^t E(t')e^{-i(\omega_g - \omega_n)t'}dt' \tag{3.20}$$

To solve this we

- calculate the fourier-transformed of $E(t) = \int_{-\infty}^{\infty} \mathfrak{E}(\omega)e^{i\omega t}d\omega$. The population at $t \to \infty$ (after the pulse) is calculated from

$$c_n(\infty) = -i < n|z|0 > \int_{-\infty}^{\infty} d\omega\, \mathfrak{E}(\omega) \underbrace{\int_{-\infty}^{\infty} dt' e^{i\omega - (\omega_g - \omega_n)t'}}_{\delta(\omega - (\omega_g - \omega_n)} \tag{3.21}$$

what yields the result we have already used in 3.4

$$c_n = -i < n|z|g > \mathfrak{E}(\omega - (\omega_g - \omega_n)) \tag{3.22}$$

- In case of a monochromatic laserpulse $E(t) = E_0 cos(\omega t) * rect(o, T)$ we derive from (3.20) in the rotating wave approximation

$$c_n(t) = -\frac{i}{2} < n|z|0 > E_0 \int_0^t (e^{i\omega - (\omega_g - \omega_n)t'} dt' \tag{3.23}$$

what leads for $t > T$ to $c_n(t) = c_n$

$$c_n = -\frac{1}{2} < n|z|0 > E_0 \frac{1}{\omega + \omega_g - \omega_n} (e^{i(\omega - \omega_g + \omega_n)T} - 1) \tag{3.24}$$

3.7 Auger-decay

While this electron remains in the Rydberg state as a so called spectator electron, the coulomb interaction V between two lower-lying electrons $|a >$ and $|b >$ results in an Auger decay. At the level of approximation, that was used for the calculation of these states, this potential V was not considered yet. We include it now and thus search for eigenstates of the new hamiltonian

$$H = H^+ + V \tag{3.25}$$

There exist several alternative paths for solving this problem. To derive a analytic result all of them need some approximations. Two of these possibilities are presented:

3.7.1 Solving by formal integration

Starting from the hole-state $e^{-iE_{[h]}t}|[h] >$ the system will decay to the final state $e^{-iE_f t}|f >$ ($E_{[h]}$ and E_f are the corresponding eigenvalues to H^+). We thus make an ansatz [26]

$$|\Psi >= c_{[h]}(t) e^{-iE_{[h]}t}|[h] > + \int c_f(t) e^{-iE_f t}|f > dk \tag{3.26}$$

where $|[h] >= |a > |b >$ and $|f >= |g > |k >$ (k is the free state $|k >= e^{ikr}$) Inserting this into the Schrödinger equation and projecting the original states onto it leads to:

$$\dot{c}_{[h]}(t) = -i \int < [h]|V|f > c_f(t) e^{-i(E_f - E_{[h]})t} dk \tag{3.27}$$

$$\dot{c}_f(t) = -i < f|V|[h] > c_{[h]}(t)e^{-i(E_{[h]}-E_f)t} \tag{3.28}$$

A formal integration results in

$$c_f(t) = -i \int_0^t < f|V|[h] > c_{[h]}(t')e^{-i(E_{[h]}-E_f)t'}dt' \tag{3.29}$$

We substitute this result into (3.27) and derive

$$\dot{c}_{[h]}(t) = -\int dk| < [h]|V|f > |^2 \int_0^t c_{[h]}(t')e^{-i(E_{[h]}-E_f)(t'-t)}dt' \tag{3.30}$$

To solve this we have to make some approximations: First of all we have to get rid of the $c_{[h]}(t)$ under the integral. This can be done under the assumption that it is a slowly varying function of time, what permits us to pull it out of the integral:

$$\dot{c}_{[h]}(t) = -c_{[h]} \underbrace{\int dk| < [h]|V|f > |^2 \int_0^t e^{-i(E_{[h]}-E_f)(t'-t)}dt'}_{p(t)} \tag{3.31}$$

This differential equation is solved by

$$c_h(t) = e^{-\int_{t'}^t p(x)dx} \tag{3.32}$$

and the time-integral in p(t) can be executed

$$p(t) = \int k^2 dk| < [h]|V|f > |^2 e^{i(E_{[h]}-E_f)t} \frac{e^{-i(E_{[h]}-E_f)t} - 1}{i(E_{[h]} - E_f)} \tag{3.33}$$

where the k^2 comes from the transformation to spherical coordinates $d^3k = k^2 dk$. A Taylor-expansion of the exponent shows us that there is no need to worry about poles. The final energy consists of $E_f = k^2/2 - E_a - E_b - E_0$. With help of $dE_f = kdk$ we transform the integral into an integration over E_f

$$p(t) = \int kdE_f| < [h]|V|f > |^2 \frac{1 - e^{i(E_{[h]}-E_f)t}}{i(E_{[h]} - E_f)} \tag{3.34}$$

As p is in the exponent of (3.32) we are interested in the real and imaginary part of it separately. Therefore we expand $1 - e^{i(E_{[h]}-E_f)t} = [1 - cos(E_{[h]} - E_f)t] + [isin(E_{[h]} - E_f)t]$. In the real part of it

$$Re(p(t)) = \int kdE_f| < h|V|f > |^2 \frac{sin(E_h - E_f)t}{i(E_h - E_f)} * \frac{t}{t} \tag{3.35}$$

we substitute $x = (E_{[h]} - E_f)t; \quad dx = -dE_f t$. We collect k, what resembles somehow a density of states, and $| < h|V|f > |^2$ to $F(E_f)$

$$Re(p(t)) = \int_{E_{[h]}t}^{\infty} dx \frac{sinx}{x} F(E_{[h]} - x/t) \tag{3.36}$$

To be able to calculate further we have to specialize on

$$E_{[h]}t \gg 1 \tag{3.37}$$

In this case we may neglect the time-dependence of F. (3.36) simplifies to

$$Re(p(t)) = F(E_{[h]}) \int_{E_{[h]}t}^{\infty} dx \frac{sinx}{x} \tag{3.38}$$

This integral can be evaluated

$$Re(p(t)) = F(E_{[h]}) \frac{\pi}{2} \tag{3.39}$$

This real part characterizes the exponential decay of $c_{[h]}$ and we therefore set it to

$$Re(p(t)) = \Gamma/2 \tag{3.40}$$

The imaginary part of p(t) can not be calculated as $\int \frac{1-cosx}{x}$ leads to a divergent integral but it can be seen from numerical results that it is rather small [26]. We will label it's result $Im(p(t)) = \Delta$. It's value is of no great importance as it cancels out in the instant the squared absolute value is taken.

All in all we obtain

$$c_h = e^{-\Gamma/2 * t + i\Delta t} \tag{3.41}$$

3.7.2 Solving by Laplace transformation

The same problem will now be solved in a different way, which makes some different approximations and seems to me to be more evident. As usual we start with an ansatz

$$|\Psi(t) >= c(t) e^{-i(E_a + E_b)t} |a, b > + \int c_c(E'_c, t) e^{-iE'_c t} |c > dE'_c \tag{3.42}$$

Inserting into the Schrödinger equation

$$i \cdot |\Psi(t) > = H|\Psi(t) >; \tag{3.43}$$

leads to two coupled differential equations for the coefficients

$$\dot{c} = -i \int dE'_c < a, b|V|c > c_c e^{-i(E'_c-(E_a+E_b)t} dE'_c \tag{3.44}$$

$$\dot{c}_c = -ic < c|V|a, b > e^{-i(E_a+E_b-E'_c)t} \tag{3.45}$$

For the sake of brevity we introduce a short notation:

$$< a, b|V|c >= V_{ab,c} \tag{3.46}$$

To solve the system we integrate (initial value $c_c(0) = 0$) and derive

$$c_c = -iV_{ab,c} * \int_0^t c(t')e^{-i(E_a+E_b-E_c)t'} dt' \tag{3.47}$$

This will be solved by Laplace transformation

$$\mathcal{L}(c(t)) = u(S) := \int_0^\infty e^{-st} c(t) dt \tag{3.48}$$

We apply the transformation rule:

$$\mathcal{L}(\dot{c}(t)) = \int_0^\infty e^{-st} \dot{c}(t) dt = su(s) - 1 \tag{3.49}$$

to (3.45) and obtain

$$\begin{aligned}(su(s) - 1) &= \int_0^\infty dt e^{-st} \int dE'_c V_{abc} \int_0^t dt' c(t') e^{-i(E_a+E_b-E'_c)(t'-t)} V_{ab,c} \\ &= \int dE'_c |V_{ab,c}|^2 \underbrace{\int_0^\infty dt e^{-st} \int_0^t dt' c(t') e^{-i(E_a+E_b-E'_c)(t'-t)} V_{ab,c}}_{\frac{u(s)}{s-i(E_a+E_b-E'_c)}}\end{aligned} \tag{3.50}$$

Rearranging results in

$$u(s) = \left(s + \int dE'_c \frac{|V_{ab,c}|^2}{s - i(E_a + E_b - E'_c)} \right)^{-1} \tag{3.51}$$

Now we make an "educated guess" for the solution. This ansatz is motivated by the result of section 3.7

$$c(t) = e^{\frac{-\Gamma}{2}t - i\Delta t} \tag{3.52}$$

It's Laplace transformed is

$$u(t) = \frac{1}{s + \frac{\Gamma}{2} + i\Delta} \tag{3.53}$$

Comparing this to (3.51) results in

$$s + \int dE'_c \frac{|V_{ab,c}|^2}{s - i(E_a + E_b - E'_c)} = s + \frac{\Gamma}{2} + i\Delta \tag{3.54}$$

- Now we try to find the zeros of the left side of the equation with help of the Banach fixed-point theorem. The corresponding iteration is:

$$s_{n+1} = -\int dE'_c \frac{|V_{ab,c}|^2}{s_n - i(E_a + E_b - E'_c)} \tag{3.55}$$

  For initial value we choose $s_0 = 0$ and iterate once

$$s_1 = -\lim_{s\to 0+} \int dE'_c \frac{|V_{ab,c}|^2}{s - i(E_a + E_b - E'_c)} \tag{3.56}$$

- Now we set the right side of (3.54) zero

$$O = s + \frac{\Gamma}{2} + i\Delta) \tag{3.57}$$

- Finally we equate (3.56) to (3.57) and obtain

$$-\lim_{s\to 0+} \int dE' \frac{|V_{ab,c}|^2}{s - i(E_a + E_b - E'_c)} = -\frac{\Gamma}{2} - i\Delta \tag{3.58}$$

The problem of the possible singularity under the integral can be circumvented by replacing the integrand by a Cauchyschen principal value P and a residuum.

$$\lim_{s\to 0+} \frac{1}{x + is} = \frac{P}{x} - i\pi\delta(x) \tag{3.59}$$

Considering this we derive

$$-\frac{\Gamma}{2} - i\Delta = \int dE'_c \frac{-i|V_{ab,c}|^2}{(E_a + E_b - E'_c)} - \pi \int dE'_c |V_{ab,c}|^2 \delta(E_a + E_b - E'_c) \tag{3.60}$$

Comparing the real (imaginary) part on both sides leads to

$$\Gamma = 2\pi |V_{ab,c}|^2 \tag{3.61}$$

and

$$\Delta = \int dE \frac{|V_{ab,c}|^2}{E_a + E_b - E'_c} \tag{3.62}$$

3.7.3 Calculation of $c_f(t)$

According to (3.29) we obtain $c_f(t)$ from

$$c_f(t) = -i < f|V|[h] > \int_0^t dt' c_{[h]}(t') e^{-i(E_{[h]}-E_f)t'} \tag{3.63}$$

Which yields when $c_{[h]}(t) = e^{-(\Gamma/2+i\Delta)t}$ is taken into account

$$c_f(t) = i < f|V|[h] > \frac{e^{-(\Gamma/2+i(\Delta+E_{[h]}-E_f)t} - 1}{\Gamma/2 + i(\Delta + E_{[h]} - E_f)} \tag{3.64}$$

For later purpose we calculate the squared absolute value:

$$|c_f(t)|^2 = | < f|V|[h] > |^2 \frac{1}{\Gamma^2/4 + (\Delta + E_{[h]} - E_f)^2} \left[1 + e^{-\Gamma t} - 2e^{-\frac{\Gamma}{2}t} cos((\Delta + E_{[h]} - E_f)t)\right] \tag{3.65}$$

3.8 A simple model for the time evolution of the shake process of the bound spectator electron

The next step is the shake-process. The preceding chapters supply all the required data we need to calculate the shake process in the time-domain: From section 3.6 we know a formula for the distribution of $|\tau >$ and section 3.7 offers a formula for the time-development of the Auger-process which causes the change of potential seen by the spectator. In this model we replace the real process of an escaping Auger electron by the creation of a hole. The spectator electron is subject to the following hamiltonian:

$$H = H^+ * |c_h|^2(t) + H^{++} * (1 - |c_h|^2(t)) \tag{3.66}$$

From this we expect the eigenvalues of H to mutate from eigenvalues of H^+ into eigenvalues of H^{++}. To calculate the shake process $< n|n' >$ we could try to represent the distribution of the new eigenstates $|n' >$ in the old eigenstate-system:

$$H^{++} = H^+ + V_{hole} \tag{3.67}$$

where $V_{hole}(t)$ is the additional potential caused by the hole in state $|a >$ that is created as a consequence of the disappearance of the Auger electron

$$V_{hole}(t) = V_{hole} * (1 - |c_h|^2) = \frac{-1}{|r_\tau - r_{|a>}|} * (1 - |c_h|^2) \tag{3.68}$$

This leads to an intuitive equation:

$$H = H^{+} + V_{hole} * (1 - |c_h|^2) \tag{3.69}$$

The more evident and strait forward path is to execute the calculations making use of the final states (eigenstates of H^{++}) right from the beginning: The hamiltonian H must for $t \to \infty$ converge to H^{++} and show the time dependence of the Auger decay for times $t \gtrapprox 0$. These considerations justify the following hamiltonian

$$H = H^{++} - V_{hole} * |c_h|^2(t) \tag{3.70}$$

We assemble the solution of

$$i\dot{\tau'} = H\tau' \tag{3.71}$$

from eigenvalues $|n'>$ of H^{++}

$$|\tau'(t)> = \sum_{n'} c_{n'}(t)|n'> e^{-iE_{n'}t} \tag{3.72}$$

Combining (3.72) and (3.71) guides us to

$$\dot{c}_{n'}(t) = -i \sum_{m'} < n'|V_{hole} * |c_h(t)|^2|m'> e^{-i(E_{m'} - E_{n'})t} c_{m'}(t) \tag{3.73}$$

We formally integrate this and derive

$$c_{n'}(t) = c_{n'}(0) - i \sum_{m'} \int_0^t dt' < n'|V_{hole}|m'> |c_h(t')|^2 e^{-i(E_{m'} - E_{n'})t'} c_{m'}(t') \tag{3.74}$$

The values at t=0 are fixed by $|\tau'(0)> = |\tau(0)>$

$$|\tau'(0)> = \sum_{n'} c_{n'}(0)|n'> = |\tau(0)> = \sum_{n} c_n(0)|n> \tag{3.75}$$

Projecting $|n'>$ onto it leads up to

$$c_{n'}(0) = \sum_{n} c_n(0) \underbrace{< n'|n>}_{shake} \tag{3.76}$$

what resembles the shake process explained in section 3.2. (3.74) can be rewritten

$$c_{n'}(t) = c_{n'}(0) - i \int_0^t dt' |c_h(t')|^2 < n'|V_{hole}| \underbrace{\left(\sum_{m'} c_{m'}(t') e^{-iE_{m'}t'} |m'> \right)}_{|\tau'>} e^{iE_{n'}t'} \tag{3.77}$$

This equation could be solved numerically by iteration. Instead of $c_{m'}(t)$ we insert $c_{m'}(0)$ and iterate. The approximation of $|\tau' >$ in (3.77) by $|\tau >$ (where the c_n do not depend on the time) allows us to calculate further analytically.

$$c_{n'}(t) = c_{n'}(0) - i \int_0^t dt' |c_h(t')|^2 < n'|V_{hole}| \underbrace{\left(\sum_n c_n e^{-iE_n t'} |n> \right)}_{|\tau>} e^{iE_{n'} t'} dt' \tag{3.78}$$

We rewrite this

$$c_{n'}(t) = c_{n'}(0) - i \sum_n c_n < n'|V_{hole}|n > \int_0^t dt' |c_h(t')|^2 e^{-i(E_n - E_{n'})t'} dt' \tag{3.79}$$

Taking $|c_h(t')|^2 = e^{\Gamma t'}$ into consideration we are capable to execute the integration and thus have

$$c_{n'}(t) = \sum_n c_n \left[< n'|n > - i < n'|V_{hole}|n > \frac{1 - e^{-[\Gamma + i(E_{m'} - E_{n'})]t}}{\Gamma + i(E_{m'} - E_{n'})} \right] \tag{3.80}$$

The influence on the Auger electron may be calculated according to the law of energy-conservation $\varepsilon_A = \omega - \varepsilon - I_{[f][f']}$. ($I_{[f][f']}$ is the change of energy of the remaining core)

3.9 Finite escape time

This time we want to consider the path R(t) the Auger-electron takes on it's way from it' original state $|a >$ at $R = r_a$ to infinity and consider it's influence on the shake process. This additional perturbation is often refereed to as "kick process". The calculation of the solution of this partial problem would still be a two-electron one and we would have to make a product-ansatz:

$$|\Psi >= \underbrace{\left[\sum_{n'} c_{n'}(t) |n'(r) > e^{-iE_{n'}t} \right]}_{\text{spectator electron } |\tau'>} * \underbrace{\left[\int dk c_k(R,t) |k(R) > e^{-iE_k t} \right]}_{\text{free Auger electron}} \tag{3.81}$$

This leads to the following differential equation for the joint probability

$$\dot{(c_{m'} c_l)} = -i \sum_{n'} \int dk [c_{n'} c_k] e^{-i(E_{n'} + E_k - E_{m'} - E_l)t} < m' < l|V_c|n' > k > \tag{3.82}$$

To reduce this problem to a one-electron-problem we have to make some more approximations: We assume the Coulomb interaction to take effect only on the spectator but not on the Auger electron. It's perturbation is considered like in the previous section in a next step according to the law of energy-conservation. To start with we calculate an averaged location of the Auger electron. This expectation value is given by $< \varepsilon_A|R|\varepsilon_A >$, ($|\varepsilon_A >= \int c_f(t)e^{-iE_f t}|f > dk$) The hamiltonian for the spectator electron is

$$H = H^{++} + \underbrace{\frac{1}{|< R(t) > -r|}}_{V_{es}(t)} \tag{3.83}$$

(r = radial location of the spectator). The following steps are just the same like (3.71) to (3.77) but with V_{es} instead of $V_{hole}|c_h(t)|^2$.

$$c_{n'}(t) = c_{n'}(0) - i\sum_{m'}\int_0^t dt' < n'|V_{es}(t)|m' > e^{-i(E_{m'}-E_{n'})t'}c_{m'}(t') \tag{3.84}$$

In [27] the electrons path was assumed to be along the z-axis starting in the origin and the influence of the kick-process was calculated. The results can be seen in figure 3.8.

3.10 Post collisional interaction (PCI)

The first experimental evidence for PCI was found and interpreted by Barker and Berry in 1966.

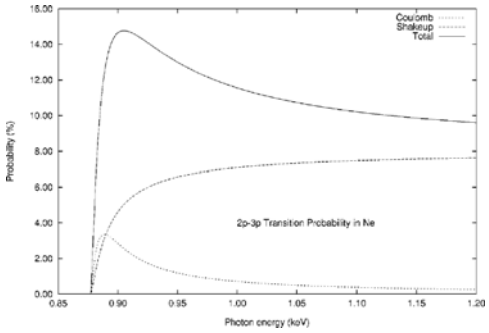


Figure 3.8: finite escape

3.10.1 The three possible cases

We will now study the case of excitation to the continuum. Three different cases have to be distinguished:

1. Excitation far above threshold: The photoelectron is fast and will never be overtaken by the Auger electron (or at least not within a time where any relevant Coulomb interaction may take place) This is the normal Auger decay as described in section 3.1.2

2. The excitation is to just close above threshold [15]: The Photoelectron will not have moved away far when it is overtaken by the Auger electron. The photoelectron feels a subsiding screening and the modified, stronger core-attraction causes it to be recaptured to a bound high-lying level (fig 3.9). ("shake down" from continuum to a bound state) The Auger electron is exposed to a weaker core attraction leading to distortion of the Auger line shape and raising of the Auger energy at the expense of the photoelectron-energy.

3. Intermediate excitation: The Auger electron overtakes the photoelectron but this one has already moved too far away to be recaptured. Both line shapes will be distorted (Auger's raised, photo's lowered). In this case we have two indistinguishable electrons of similar energy that impinge on the detector [28]. Therefore the cross section for observing either photo- or Auger electrons at energyε_e is [29]

$$\frac{d^2\sigma}{d\varepsilon_e} \propto \sum [\Gamma(\varepsilon_e)| < E' - \varepsilon_e|\tau > |^2 + \Gamma(E' - \varepsilon_e)| < \varepsilon_e|\tau > |^2] \quad (3.85)$$

where $E' = \omega - I_{[f][f']} = E_{exc} + \varepsilon_A$ $I_{[f][f']}$ is the increase in energy from the original neutral to the doubly ionized state (hole in orbital f and f'). $\Gamma(x)$ represents the Auger-decay to an Auger electron energy x. The

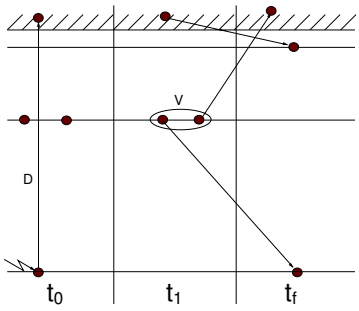


Figure 3.9: Recapture of the photoelectron

PCI line shape seems to be independent from the atomic structure. The only significant parameters are the excess energy and the intermediate lifetime Γ^{-1}.

Outside the ionic core the real and imaginary part of the intermediate state $|\tau_0>$ attain the form of a damped oscillating wave as a function of the radial distance r [22]. The damping factor $e^{-\frac{r}{r_0}}$ where $r_0 \approx 2\Gamma\sqrt{2E_{exc}}$ determines how far the photoelectron has proceeded from the ion before shake-down into a discrete or continuous state takes place.

Chapter 4

Fano process

4.1 Introduction

In 1935 Beutler observed autoionizing states as broad and asymmetric lines in the photo absorbtion spectra of argon, krypton and xenon. In the same year developed Ugo Fano [1] [30] a theory for it which was first published in "Nuovo Cimento" but is better known in the extended form that he published in the Physical Review [1] in 1961, which is still among the journals most cited papers. Its simple 'Fano profile' formula, which predicts the shape of spectral lines, has been a workhorse of nuclear, atomic, molecular and condensed-matter physics. The impact of this work has been conceptually important since any decay problem can be formulated as an interaction between discrete and continuous states whether photon, phonon, exciton etc. manifolds.

4.2 Basic interaction mechanism

If an atom is exposed to radiation it may happen that an electron is removed from the core. There exist mainly two different escaping-paths (figure 3.10): Either one of the outer electrons is removed in a single step or an inner-shell electron is excited to an outer shell where it undergoes an subsequent auger decay, leading to the same final state. These two possibilities are often referred to as channels. These two alternative paths interfere and lead to the characteristic asymmetric crossection of the Fano profile (figure 3.11). We can observe all the characteristics of a resonance in energy: The scattering cross section grows in its vicinity, the scattering phase varies rapidly as a function of energy, the density of the wave function $|\Psi(x) >$ is strongly enhanced

[1] Ugo Fano; 1912-2001

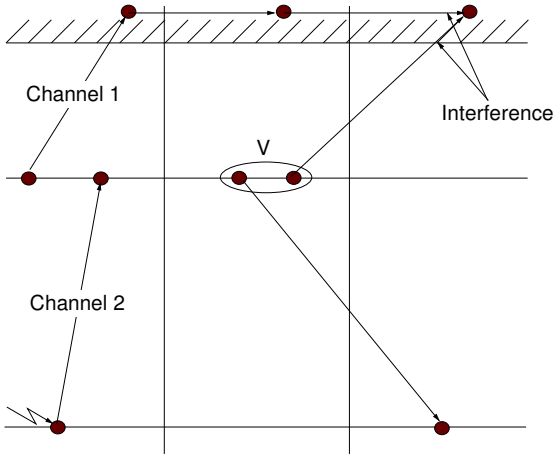


Figure 4.1: The Fano process

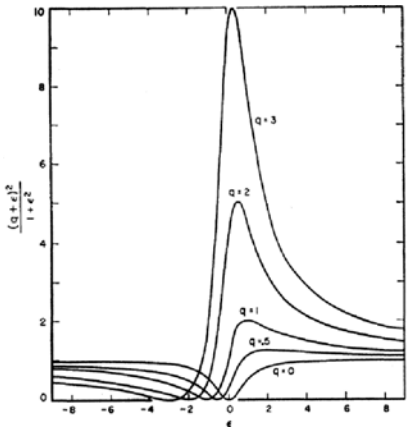


Figure 4.2: The Fano-profile

at small distances. Experimentally autoionizing states can be observed via different channels

- Photo absorbtion and photo electron spectrometry
- inelastic scattered electrons
- spectrometry of autoionizing electrons

4.3 Changing from a two-particle description to a one-particle one

In the preceding section the Fano-process is explained as a two particle process. This corresponds to reality but makes calculation rather difficult. This can be circumvented by introducing a one-particle description (see: fig 3.12). The new one-particle-hamiltonian is

$$\tilde{H} = H_0 + V + D \tag{4.1}$$

where V is a Coulomb interaction which represents the Auger-decay-mechanism, D is the dipole matrix for the laser-excitation and H_0 is the undisturbed hamiltonian with a discrete and a continuum set of single-particle orthonormal eigenfunctions, which are coupled through the (configuration-) interaction V. These eigenstates are:

- The initial bound groundstate : $|g>$
- The discrete excited bound state: $|a>$, which will be referred to as autoionizing state and resembles in the two particle description the intermediate hole-state

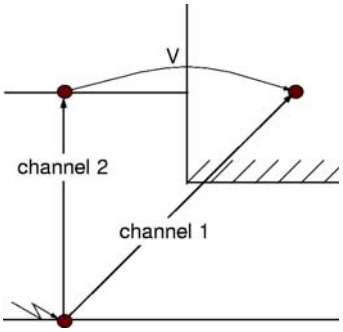


Figure 4.3: One-particle representation of the Fano-process

- and the set of continuum wavefunctions: $|c(E)>$. These asymptotically stationary standing waves are orthonormal: $< c(E')|c(E) >= \delta(E' - E)$

where the corresponding eigenvalues are:

$$H_0|g >= E_g|g > \tag{4.2}$$

$$H_0|a >= E_a|a > \tag{4.3}$$

$$H_0|c >= E_c|c > \tag{4.4}$$

The discrete energy E_a lies above at least the first ionization threshold in the energy range of the continuum. It is bound only in some approximation that neglects its interaction V with the continuum in which it is embedded [31]. This additional potential causes this state to be unstable against ionization with one electron being ejected. The exact coincidence of energies of different configurations, E_a and a specific E_c, makes it impossible to treat this problem with conventional perturbation theory.

4.4 Derivation of the Fano-formula[1]

To get a deeper understanding of the problem it is convenient to introduce the projection-operators:

$$P = |g >< g| \qquad Q = |a >< a| + \int dE_c |c >< c| \tag{4.5}$$

Together they form a complete system:

$$P + Q = 1 \tag{4.6}$$

We can use them to rewrite (3.86)

$$\tilde{H} = \underbrace{(P+Q)}_{1}\tilde{H}\underbrace{(P+Q)}_{1} = P\tilde{H}P + P\tilde{H}Q + Q\tilde{H}P + Q\tilde{H}Q \tag{4.7}$$

The following abbreviations and assumptions will be used:

$$< c|\tilde{H}|a >=< c|Q\tilde{H}Q|a >=< c(E_c)|V|a >:= V_{ca}(E_c) \tag{4.8}$$

This variable indicates how strong the bound state is coupled to the continuum and will therefore have a strong influence on the decay process

$$< a|\tilde{H}|g >=< a|Q\tilde{H}P|g >=< a|D|g >:= D_{ag} \tag{4.9}$$

$$< c|\tilde{H}|g >=< c|Q\tilde{H}P|g >=< c(E)|D|g >:= D_{cg}(E) \tag{4.10}$$

$$< c|V|g >= 0 \qquad < c|V|c' >= 0 \tag{4.11}$$

The eigenvalue-problem thus yields:

$$\begin{pmatrix} H_0 & D_{ag} & D_{cg} \\ D_{ga} & H_0 & V_{ac} \\ D_{gc} & V_{ac} & H_0 \end{pmatrix} * \begin{pmatrix} |g> \\ |a> \\ |c> \end{pmatrix} = \begin{pmatrix} E_g \\ E_a \\ E_c \end{pmatrix} * \begin{pmatrix} |g> \\ |a> \\ |c> \end{pmatrix} \tag{4.12}$$

The $\tilde{H}$-matrix can be rewritten:

$$\begin{pmatrix} P\tilde{H}P & Q\tilde{H}P \\ P\tilde{H}Q & Q\tilde{H}Q \end{pmatrix} \tag{4.13}$$

We want to solve this problem in two steps. First we try to diagonalize the submatrix $H = Q\tilde{H}Q$ and search for it's eigenstates. Afterwards we use its result to solve the whole problem.

Diagonalization requires the solution of

$$H|\Psi(E) >= E|\Psi(E) > \tag{4.14}$$

We make the following ansatz

$$|\Psi_E >= c_a(E)|a > + \int dE' c_c(E')|c(E') > \tag{4.15}$$

The energy dependance will from now on only be indicated if necessary. Inserting this into (3.99) and projecting $|a>$ or $|c>$ onto it leads up to

$$E_a c_a + \int dE' V^*_{ca}(E') c_c(E') = E c_a \tag{4.16}$$

$$V_{ca}(E') c_a + E' c_c = E c_c \tag{4.17}$$

we use (3.102) to calculate c_c

$$c_c = \frac{V_{ca}(E') c_a}{E - E'} \tag{4.18}$$

In a next step we want to insert this into (3.101) and are confronted with a problem of a singularity at $E' = E$. This problem can either be circumvented by quantization of the continuum [9] or, like Fano did, by applying the pole approximation[2]. We obtain for the formal solution

$$c_c = V_{ca}(E') c_a \left(\frac{P}{E - E'} + z(E)\delta(E - E') \right) \tag{4.19}$$

[2]Pole approximation: We replace the fraction under the integral by an principal part (indicated by P) plus a weighted delta-pulse at the pole. The principal part for a pole at 0 is defined by : $P\int_a^b := \lim_{\varepsilon \to 0} \int_a^{-\varepsilon} + \int_\varepsilon^b$

where the weighting function z(E) is to be determined later. The continuum-wavefunctions have the following free asymptotic behavior:

$$|c(E') >= sin(k(E')r + \delta) \tag{4.20}$$

Now we are capable to calculate the integral of (3.101).

$$\int dE' c_c |c > \propto sin(k(E)r + \delta + \Delta(E)) \tag{4.21}$$

where

$$\Delta(E) = -arctan(\frac{\pi}{z(E)}) \tag{4.22}$$

This phase-shift is due to the configuration-interaction of $|c>$ and $|a>$. To calculate z(E) we insert (3.100) into (3.101), factor out c_a and derive

$$z(E) = \frac{E - E_a - F(E)}{|V_{ca}(E)|^2} \tag{4.23}$$

where

$$F(E) = P \int dE' \frac{|V_{ca}(E')|^2}{E - E'} \tag{4.24}$$

We take this result to evaluate (3.107) and obtain the for a resonance typical behavior: The phase shift varies by π as E traverses an Interval $|V_{ca}|^2(E)$ about the shifted resonance at

$$\bar{E}_a := E_a + F \tag{4.25}$$

The coefficient c_a can now be calculated from the normalization of (3.100).

$$< \Psi(\overline{E})|\Psi(E) >= c_a * (\overline{E}) c_a(E) + \int d\tilde{E} c_c * (\overline{E}) c_c(E) = \delta(\overline{E} - E) \tag{4.26}$$

Substituting (3.104) and evading the problem of the occurring poles with help of the pole approximation (for details see [17]) brings us to:

$$\begin{aligned} c_a(E) =& \frac{sin\Delta(E)}{\pi V_{ca}(E)} = \frac{1}{\pi V_{ca}(E)} \sqrt{\frac{tan^2\Delta}{1 + \tan^2\Delta}} \\ =& \frac{1}{\pi V_{ca}(E)} \frac{\Gamma(E)/2}{(E - E_r)^2 + \Gamma^2(E)/4} \end{aligned} \tag{4.27}$$

$$\begin{aligned} c_c(E') =& P \frac{V_{ca}(E')|sin\Delta}{\pi V_{ca}(E)(E - E')} - cos(\Delta)\delta(E - E') \\ =& sin\Delta \left[\frac{|V_{ca}(E')|}{\pi V_{ca}(E)(E - E')} + \frac{E - E_r}{\pi |V_{ca}(E)|} \delta(E - E') \right] \end{aligned} \tag{4.28}$$

where we have defined a variable $\Gamma(E)$ that characterizes the spectral width of the autoionizing state:

$$\Gamma(E) = 2\pi V_{ca}(E) \tag{4.29}$$

The eigenfunction Ψ can now be calculated:

$$|\Psi_E >= \frac{sin\Delta}{\pi V_{ca}(E)}|\Phi > -cos\Delta|c(E) > \tag{4.30}$$

where the discrete state $|a>$ is replaced by a broader and shifted state

$$|\Phi_E >= |a> + P\int dE' \frac{V_{ca}(E')}{E - E'}|c> \tag{4.31}$$

Now we use these results to solve the whole excitation-decay-problem. We calculate the excitation-probability given by $|<\Psi|T|g>|^2$ where T is any excitation-operator.

$$<\Psi|T|g>= \frac{T_{\Phi g}}{\pi V_{ca}} sin\Delta - T_{cg}cos\Delta \tag{4.32}$$

where

$$T_{\Phi g} =<\Phi|T|g> \quad and \quad T_{cg} =<c|T|g> \tag{4.33}$$

Δ is a function of E and varies sharply at resonance. As $sin\Delta$ is a even function of $E - E_a - F$ and $cos\Delta$ an odd one they interfere in (3.117) with opposite phase on the two sides of the shifted resonance. From (3.117) we can calculate the energy for which the transition probability vanishes $tan\Delta_0 = \frac{\pi V T_{cg}}{T_{\Phi g}}$ (see fig: 3.11)

It is convenient to introduce the ratio

$$q := \frac{T_{\Phi g}}{\pi V_{ca}^* T_{cg}} \tag{4.34}$$

$0,5\pi q^2 = \frac{|<\Phi|T|g>|^2}{|<c|T|g>|^2\Gamma}$ is the ratio of transition probabilities from the ground state $|g>$ to the modified discrete state and to a band with Γ of unperturbed continuum states. Furthermore we define a reduced energy variable

$$\epsilon := -cot\Delta = \frac{E - \bar{E}_a}{\frac{1}{2}\Gamma} \tag{4.35}$$

Using these variables we obtain the Fano-curve for the ratio of transition to the modified continuum or to the undisturbed continuum:

$$\frac{|<\Psi|T|i>|^2}{|<c|T|i>|^2} = \frac{(q+\epsilon)^2}{1+\epsilon^2} = 1 + \frac{q^2 - 1 + 2q\epsilon}{1+\epsilon^2} \tag{4.36}$$

This formalism can be expanded to more than one discrete state or/and to several continua. [1]

4.5 Time-dependent analysis [2]

Now we have calculated the involved states and know about their influence on the measured spectra. In the following we want to study the time development of the process. From now on $\bar{E}_a$ will indicate the shifted resonance $\bar{E}_a = E_a + F$. We model the excitation radiation as monochromatic

$$T = D = z(\mathcal{E}e^{i\omega t} + \mathcal{E}e^{-i\omega t}) \tag{4.37}$$

The hamiltonian under study is still (3.86)

$$H = H_0 + V + D \tag{4.38}$$

We start with an ansatz with time dependant coefficients:

$$|\Upsilon(t)>= c_g(t)|g> + \int dE' c_\Psi(t)|\Psi> \tag{4.39}$$

where $|\Psi>$ is the Fano state we have calculated above. At the beginning t=0 the atom is in the ground state $|g>$. We insert this into the Schrödinger equation and project $<g|$ or $<\Psi|$ onto it.

$$\dot{c}_g = -iE_g c_g - i\int dE' <g|PHQ|\Psi> c_\Psi(t) \tag{4.40}$$

$$\dot{c}_\Psi = -iE' c_\Psi - i <\Psi|QHP|g> c_g \tag{4.41}$$

To make calculation a bit easier we change to the interaction picture by setting

$$v_g(t) = c_g e^{iE_g t} \quad and \quad v_\Psi = c_\Psi e^{iE_\Psi t} \tag{4.42}$$

Now we apply the Rotating-wave approximation [3]:

$$\dot{v}_g(t) = -i\int dE' M^*_{E'g}\mathcal{E}e^{i(\omega - E' + E_g)t} v_\Psi \tag{4.43}$$

$$\dot{v}_\psi = -iM_{E'g}\mathcal{E}^* e^{-i(w - E' + E_g)t} v_g \tag{4.44}$$

where

$$M_{E'g} =<\Psi|z|g>= (\frac{D_{\Phi g}}{V^*_{ca}} sin(\Delta) - D_{cg} cos\Delta) \tag{4.45}$$

[3]The Rotating wave approximation: Whenever two sin-functions are multiplied, $sin(\omega_1 t)sin(\omega_2 t)$, we derive on the one hand an oscillation at the lower frequency $|\omega_1 - \omega_2|$ and on the other hand an oscillation at the higher frequency $|\omega_1 + \omega_2|$. The approximation demands to neglect the high-frequency oscillations as they are usually averaged to zero

where $D_{\Phi g} =< \Phi|z|g >$ and $D_{cg} =< c|z|g >$

The probability for ionization having taken place, P(t), at the end of the laser pulse of duration T is given by:

$$P(T) = 1 - |c_g(T)|^2 - |c_a(T)|^2 = \int dE' |c_c(T)|^2 \tag{4.46}$$

The mentioned c_a can be derived from (3.124) and (3.115)

$$c_a(t) = \int dE' \frac{c_\Psi sin(\Delta)}{\pi V_{ca}} \tag{4.47}$$

After the laser is turned off, $t > T$, there is no more excitation but still population of $|a >$ may decay and enhance P(t) still further:

$$P(t) = 1 - |U_g(T)|^2 - |U_a(T)|^2 e^{-\Gamma(t-T)} \tag{4.48}$$

Formally integrating (3.129) we derive

$$v_\Psi = -i \int_0^t dt' M_{E'g} \mathcal{E}^* e^{-i(\omega - E' + E_g)t'} v_g(t') \tag{4.49}$$

and substitute this result into (3.128) to obtain

$$\dot{v}_g = -i \int dE' |M_{E'g}|^2 |\mathcal{E}|^2 \int_0^t e^{i(\omega - E' + E_g)(t'-t)} v_g(t') \tag{4.50}$$

We try to solve this equation by Laplace transformation [4].

$$\int_0^\infty dt e^{-pt} v_g(t) = u_g(p) \tag{4.53}$$

[4] The Laplace transformation F(p) of f(t) is defined by

$$\int_0^\infty dt e^{-pt} f(t) = F(p) \tag{4.51}$$

The function f(t) must be piecewise smooth and for $t \to \infty$ it must not tend to ∞ stronger than $e^{\alpha t}$ where $\alpha > 0$. Under this conditions the Laplace integral $\mathcal{L}\{f(t)\}$ converges in the right half-space where $Re\{p\} > \alpha$
Inversion:

$$\mathcal{L}^{-1}\{F(p)\} = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dp\, e^{pt} F(p) = f(t) = \left\{ \begin{array}{ll} f(t) & t > 0 \\ 0 & t < 0 \end{array} \right\}. \tag{4.52}$$

The path for this complex integral is the parallel $Re\{p\} = c$ to the imaginary axe, where $Re\{p\} = c > \alpha$.

where the initial condition forces $u_g(0) = 1$. Equation (3.135) is transformed to

$$u_g(p) = \frac{1}{p + \int dE' \frac{|M_{E'g}|^2 |\mathcal{E}|^2}{p - i(\omega - E' + E_g)}} = \frac{1}{p + S(p)} \tag{4.54}$$

Now we set

$$p = -iz \tag{4.55}$$

where $z = x + iy$
For the integration-path we may choose the imaginary axe (see footnote 4).

$$v_g(t) = \frac{-1}{2\pi} \int_{-\infty}^{+\infty} dx\, e^{-ixt} u_g^+(x) \tag{4.56}$$

where

$$u_g^+(x) = \lim_{\eta \to 0+} u_g(x + i\eta) = \frac{i}{x - s(x) + iy(x)} \tag{4.57}$$

To simplify this we calculate (3.130) to

$$\mathcal{E}|M_{E'g}|^2 = \overbrace{\left[\underbrace{|D_{E'g}|^2 |V_{ca}|^2}_{A} + \underbrace{|D_{cg}|^2}_{C} (E - \bar{E}_a)^2 + \underbrace{|V_{ca}|^2 2Re(\frac{D_{E'g} D_{cg}}{V_{ca}})}_{B} (E - \bar{E}_a)^2 \right]}^{\gamma} * \\ * \left[(E - \bar{E}_a)^2 + \pi^2 |V_{ca}|^4 \right]^{-1} \tag{4.58}$$

With help of this we may write

$$s - iy = P \int_{-\bar{E}_a}^{\infty} dE' \frac{\gamma}{(x - E')[(E' - \bar{E}_a)^2 + \kappa^2]} - i\pi \frac{\gamma}{(x - \bar{E}_a)^2 + \kappa^2} \tag{4.59}$$

where $\kappa = \frac{\Gamma}{2}$ ($\Gamma = 2\pi |V_{ca}|^2$). Under the assumption of slowly varying matrix elements of D and V we may write $\gamma = A + B(E' - \bar{E}_a) + C(E' - \bar{E}_a)^2$, where A, B and C are energy-independent. Furthermore we replace the lower limit of the integral $\bar{E}_a$ by $-\infty$ in all but the following integral.

$$\int_{-\bar{E}_a/\kappa}^{\infty} dm \frac{m b(m)}{m^2 + 1} := N \tag{4.60}$$

where N is a pure number and b(m) is defined by B/B_0. The subscript 0 from now on indicates the function being evaluated at $E_g + \omega$. N determines the magnitude of the laser-induced stark shift of the state $|g>$ and depends

on how fast the bound-free matrix element D_{cg} goes to zero as $E_c \to \infty$. The other integrals can be approximated by the replacing A and B by A_0 and B_0.

All in all this results in

$$s(x) - iy(x) = \frac{\pi}{\kappa}\frac{A_0 + B_0 X + C_0 X^2}{X + i\kappa} - \frac{\pi}{\kappa}(B_0 + C_0 X + C_0 \kappa N) \tag{4.61}$$

where:

- $A_0 = |\mathcal{E}|^2 |D_{E'g}|^2 |V_{ca}|^2$
- $B_0 = |\mathcal{E}|^2 2Re\frac{D^*_{E'g} D_{cg}}{V_{ca}} |V_{ca}|^2$
- $C_0 = |E_0|^2 |\tilde{\mu}_{cg}|^2$
- $\kappa = \frac{\Gamma}{2}$
- $X = x + w - (\bar{E}_a - E_g)$

Now we have to calculate the inverse Laplace transformation of u_g to obtain the desired time dependence.

$$v_g(t) = \frac{-1}{2\pi i}\int_{-\infty}^{+\infty} dx \frac{e^{-ixt}}{x - s(x) + iy(x)} \tag{4.62}$$

we now introduce some generalized Rabi frequency (generalized because $D_{E'g}$ couples the ground state to Φ and not to a single discreet state). With help of

$$\Omega^2 := \frac{\pi A_0}{\kappa} = |\mathcal{E}|^2 |D_{E'g}|^2{}_{E'=\bar{E}_a} \tag{4.63}$$

and the detuning

$$\delta = \omega - (\bar{E}_a - E_g) \tag{4.64}$$

(3.147) can now be written

$$c_g(t) = \frac{1}{2\pi i}\int_{-\infty}^{+\infty} dx \frac{(x + \delta + i\kappa)e^{-ixt}}{\Lambda(x)} \tag{4.65}$$

where

$$\Lambda(x) = \left(x + \frac{\Omega^2}{q^2\kappa^2}(N\kappa + i\kappa)\right)(x + \delta + i\kappa) - \Omega^2\left(1 - \frac{i}{q}\right)^2 \tag{4.66}$$

. We now assume we know the roots: $x_\pm$ of Λ. This finally results in

$$c_g(t) = \frac{1}{x_+ + x_-}\left[(x_+ + \delta + i\kappa)e^{-ix_+ t} - (x_- + \delta + i\kappa)e^{-ix_- t}\right] \tag{4.67}$$

4.6 Alternative calculation using the resolvent operator

In section 2.4 we introduced a resolvent which is, just like the hamiltonian, capable to describe the time-evolution of the system. We now want to make use of that. The hamiltonian of the problem is $H = H_0 + V + D$ where $H_0 = H_A + H_R$ consists of an atomic H_A and a radiation H_R part. The eigenvalues are therefore $E'_g = E_g + \omega$, $E'_a = E_a$ and $E'_c = E_c$. The wavefunction has a time evolution according to

$$|\Psi >= e^{-iHt}|\Psi(0) >= U(t)|\Psi(0) >= U_{gg}|g > + U_{ag}|a > + \int dE_c\, U_{cg}|c > \tag{4.68}$$

The coefficients U_{xy} are the matrix elements of U(t) which can be calculated by the inverse Fourier-transformation of the resolvent operator G.

$$G(z) = \frac{1}{z - H} \tag{4.69}$$

$$U(t) = \frac{-1}{2\pi i} \int_{-\infty}^{\infty} dx e^{-ixt} G(x) \tag{4.70}$$

This reduces the problem to the calculation of the matrix elements of G. $G_{gg} =< g|PGP|g >$, $G_{ag} =< a|QGP|g >$ and $G_{cg} =< c|QGP|g >$. (3.154) can be rewritten

$$(z - H)\underbrace{(P + Q)}_{1} GP = P \tag{4.71}$$

Projecting P or Q onto it leads us to

$$(z - PHP)(PGP) - (PHQ)(QGP) = P \tag{4.72}$$

$$(z - QHQ)(QGP) - (QHP)(PGP) = 0 \tag{4.73}$$

Projecting suitable states onto it and making use of the definitions from the previous sections we derive

$$(z - E'_g)G_{gg} - D_{ga}G_{ag} - \int dE'_c D_{gc}G_{cg} = 1 \tag{4.74}$$

$$-D_{ag}G_{gg} + (z - E'_a)G_{ag} - \int dE'_c V_{ac}G_{cg} = 0 \tag{4.75}$$

$$-D_{cg}G_{gg} - V_{ca}G_{ag} + (z - E'_c)G_{cg} = 0 \tag{4.76}$$

This system needs to be solved. From (3.161) we obtain

$$G_{cg} = \frac{1}{z - E_c'}(D_{cg}G_{gg} + V_{ca}G_{ag}) \tag{4.77}$$

Inserting this into (3.159) and (3.160) and the solving this new system leads us to

$$G_{gg} = \frac{1}{\Lambda} \tag{4.78}$$

$$G_{ag} = \frac{D_{ag} + \int dE_c \frac{V_{ac}Dcg}{z-E_c}}{(z - E_a - \int \frac{|V_{ac}|^2}{z-E_c})\Lambda} \tag{4.79}$$

where

$$\Lambda = z - E_g - \omega - \int \frac{|D_{cg}|^2}{z - E_c} - \frac{(D_{ga} + \int dE_c \frac{D_{gc}V_{ca}}{z-E_c})(D_{ag} + \int dE_c \frac{D_{ag}}{V}_{ac} z - E_c)}{z - E_a - \int dE_c \frac{|V_{ac}|^2}{z-E_c}} \tag{4.80}$$

The occurring integrals can be evaluated under the assumption of slowly varying matrix elements. Then we replace $z \to \lim_{\epsilon\to 0} E_g + \omega + i\epsilon$ and again make a pole approximation.

$$\int dE_c \frac{|D_{cg}|^2}{z - E_c} \simeq P \int dE_c \frac{|D_{cg}|^2}{E_g + \omega - E_c} - i\pi |D_{cg}(E_g + \omega)|^2 := S_g - i\frac{\gamma_g}{2} \tag{4.81}$$

The introduced S_g and γ_g are the shift and ionization width of the state $|g>$ due to direct transitions. (compare to C_0 in the previous section)

$$\int dE_c \frac{|V_{ca}|^2}{E_g + \omega - E_c} \simeq P \int dE_c \frac{|V_{cg}|^2}{E_g + \omega - E_c} - i\pi |V_{ca}(E_g + \omega)|^2 := F_a - i\frac{\Gamma_g}{2} \tag{4.82}$$

$$D_{ag} + \int dE_c \frac{D_c g}{V}_{ac} z - E_c) \simeq D_{ag} + P \int dE_c \frac{D_c g}{V}_{ac} E_g + \omega - E_c) - i\pi (V_{ac} D_{cg})_{E_g+\omega)} := D_{Eg}(1 - \frac{i}{q}) \tag{4.83}$$

The variables are the same like introduced in the previous section.

4.7 Interpretation

4.7.1 Weak field case

As a consequence of $\Omega \ll \kappa$ in the weak-field limit we may neglect several terms and thus have to calculate the roots of:

$$x^2 + [\delta + i(1 + \beta^2)\kappa]x - [\alpha^2 - i\beta^2\kappa(\delta + i\kappa)] = 0 \tag{4.84}$$

where $\beta^2 = \frac{\Omega^2}{q^2\kappa^2}$ and $\alpha^2 = \Omega^2\left(1 - \frac{i}{q}\right)$. The roots are (again neglecting small terms)

$$x_+ = \frac{\alpha^2}{\delta + i\kappa} - i\beta^2\kappa \quad x_- = -(\delta + i\kappa) - \frac{\alpha^2}{\delta + i\kappa} + i\beta^2\kappa \tag{4.85}$$

Because of the weak field limit it is $|x_+| \ll |x_-|$ and only the exponential e^{-ix_+t} matters in (3.152). $|c_g|$ decays at a rate of $2Im(x_+)$.

4.7.2 strong field case

The strong field case is characterized by $q \to \infty$. (3.151) reduces to

$$x(x + \delta + i\kappa) - \Omega^2 = 0 \tag{4.86}$$

resulting in the roots

$$x_\pm = -\frac{1}{2}(\delta + i\kappa) \pm \Omega \tag{4.87}$$

In this case c_g develops like

$$c_g(t) = \frac{1}{2\Omega}\left[[\frac{1}{2}(\delta + i\kappa) + \Omega]e^{-i(\Omega - \frac{\delta}{2})t} - [\frac{1}{2}(\delta + i\kappa) - \Omega]e^{i(\Omega + \frac{\delta}{2})t}\right] \tag{4.88}$$

In this case we obtain the typical behavior of a state $g >$ strongly coupled to another bound state $|a >$. Like in section 2.5 the oscillation occurs at two different frequencies separated by the Rabi-frequency. Additional to that it decays at a rate of δ.

4.7.3 numerical results [2]

Lambropoulos and Zoller have shown [2] that for a weak field the transition-probability per unit of time is time-independent. For large light intensities or for short laser pulse duration it is of importance. In figure 3.13 the total ionization is plotted as a function of detuning from resonance for constant light intensities but different times of interaction. From this figure it can be deduced that as long as $T \gtrsim 5\Gamma^{-1}$ we obtain the typical auto-ionization profile with its characteristic minimum and asymmetric shape. For smaller T $T = \Gamma^{-1}$ the line shapes do not show the expected profile but it is flat.

In figure 3.14 the total ionization is plotted for a long time of interaction $T = 5\Gamma^{-1}$ and q=5 for different light intensities. For increasing intensities the maximum vanishes, the minimum-position undergoes an ac-stark-shift and the ionization probability tends to one for all detunings.

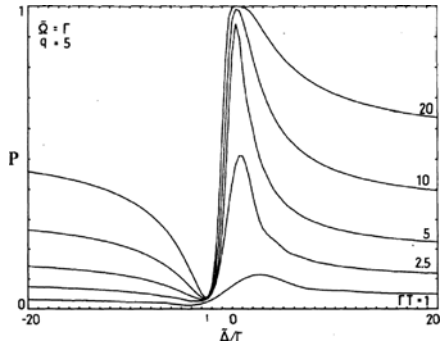


Figure 4.4: The total ionization P is plotted as a function of detuning Δ from resonance for constant light intensities but different times of interaction. [2]

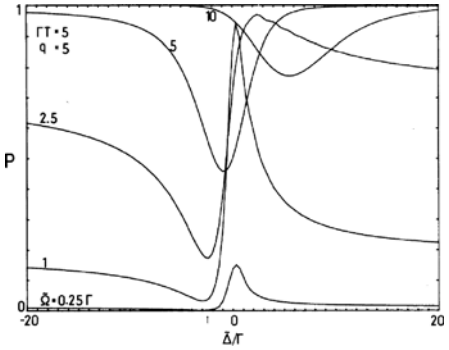


Figure 4.5: The total ionization P is plotted for $T = 5\Gamma^{-1}$ and q=5 for different light intensities. [2]

In figure 3.15 we see the behavior in relatively strong field for different moments. None of the curves shows the expected behavior. Especially the T=1-curve shows undulations due to the Rabi-oscillations between $|g>$ and $|a>$. The decay mechanism smoothes them.

Finally in figure 3.16 the time-development of the involved states and the ionization probability is presented. The Rabi-oscillations are damped due to the decay mechanism.

4.8 Using Fano's formalism to study the time dependance of the Auger-decay

In the introduction of this chapter it was claimed that Fano's derivation was a useful tool for many kinds of decay-problems. To give an example for this we now want to derive the result from section 3.7 using this procedure. The state of the interacting electrons e_1^- and e_2^- corresponds to the state $|a>$. The special kind of excitation doesn't have an influence on the decay so we may assume that the electron has always been in the exited state but the interaction V_{ac} starts at a certain time t=0. For reasons of simplicity we thus may set the initial state to $|a>$ in a hamiltonian $H_0 + V(t)$ instead of $|g>$ and $H = H_0 + D + V$. We are interested in the state at a time $T > 0$. The measured Auger electrons are better described in the eigenstates of H_0 as the coulomb interaction falls of with distance. This is implemented in our model by turning off the Interaction V just in the moment of measurement.

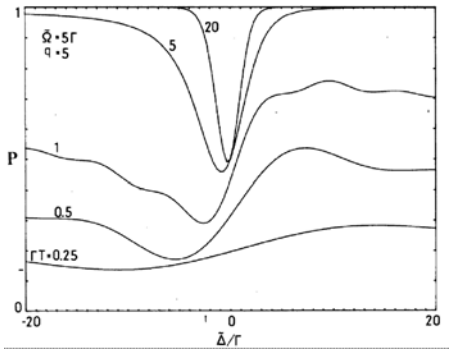


Figure 4.6: The behavior in relatively strong field for different moments is plotted. None of the curves shows the expected behavior.[2]

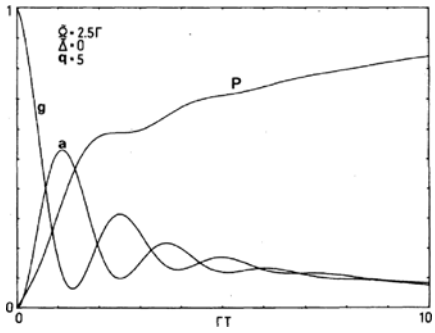


Figure 4.7: Time-development of the involved states and the ionization probability [2]

The Hamiltonian is

$$H(t) = \begin{cases} H_0 & for \quad t < 0 \\ H = H_0 + V & for \quad 0 < t < T \\ H_0 & for \quad t > T \end{cases} \tag{4.89}$$

Next we make a piecewise ansatz [17]

$$|\Psi(t)>= \begin{cases} |a> e^{-iE_a t} & for \quad t < 0 \\ \int dE_f c_f |f> e^{-iE_f t} & for \quad 0 < t < T \\ c_a|a> e^{-iE_a t} + \int dE_f c_c |c> e^{-iE_c(t-T)} & for \quad t > T \end{cases} \tag{4.90}$$

where $|f>$ resembles the Fano state. The expansion coefficients c_f, c_a or c_c are time-independent as the corresponding states are eigenstates of the "hamiltonians of their time". At t=0 and t=T continuity of the wave function must be granted.

$$|a>= \int dE_f c_f |f> \tag{4.91}$$

$$\int dE_f c_f |f> e^{-iE_f T} = c_a|a> e^{-iE_a T} + \int dE_f c_c |c> \tag{4.92}$$

To solve this system of equations we project the eigenstates onto it and obtain

$$c_f = a^* \tag{4.93}$$

where a* is given by (3.112).

$$c_a = \int dE_c \, c_f \, a \, e^{-iE_f t} \tag{4.94}$$

$$c_c = \int dE_c \, c_f \, h \, e^{-iE_f t} \tag{4.95}$$

where h is given by (3.113) The two integrals range over the permitted regions of energy, which are limited by the threshold-energy of the atom. To be capable to go on with analytical calculation we need to make an approximation. We assume the Auger electron to have an energy far from threshold so that it is justified to set the limits of the integrals to infinity.

$$E_{threshold} \to \infty \tag{4.96}$$

Under the assumption that the matrix element V_{ca} is an analytic function of energy the integrations can now be solved with help of the residue integration. Using previous results the discrete expansion coefficient follows as

$$c_a = \int_{-\infty}^{\infty} dE_c \frac{\Gamma/2\pi}{(E-E_r)^2 + {\Gamma_E}^2/4} e^{-iET} = e^{iE_rT} e^{-\Gamma_0 T/2} \tag{4.97}$$

For this integration the integration path was closed in the lower half-plane; $\Gamma_0 = \Gamma_E(E_r)$. As usual we are interested in the squared value $|c_a|^2 = e^{-\Gamma_0 T}$ what is just the result we have obtained before. It is important to remember that this resulting exponential decay is only an approximation of the real time dependence. Without the approximation (3.181) we would not have obtained an exponential decay! The continuum expansion coefficient is calculated by

$$c_c(E) \approx \int_{-\infty}^{\infty} dE_c \frac{|V_{ca}|^2}{(E-E_r)^2 + {\Gamma_E}^2/4} \left(P\frac{V_{ca}}{E_c - E} + \frac{E-E_r}{V_{ac}} \delta(E-E_c) \right) e^{-iE_cT} \tag{4.98}$$

To execute this integration we rewrite the principal value

$$P\frac{V_{ca}}{E_c - E} = \frac{V_{ca}}{E_c - E - i\epsilon} - i\pi\delta(E-E_c) \tag{4.99}$$

because a pole in the upper half plane doesn't contribute. This transforms (3.183) into

$$\begin{aligned} c_c(E) \approx \int_{-\infty}^{\infty} dE_c \frac{|V_{ca}|^2}{(E-E_r)^2 + {\Gamma_E}^2/4} \frac{V_{ca}}{E_c - E - i\epsilon} e^{-iE_cT} + \\ + \frac{V_{ca}}{(E-E_r)^2 + {\Gamma_E}^2/4} (E - E_r - i\pi {V_{ca}}^2) e^{-iE_cT} \end{aligned} \tag{4.100}$$

the integration path is closed so that only the pole at $E_c = E_r - i\Gamma/2$ contributes. With the assumption that Γ_E depends only weak on E we may replace it by Γ_0 and derive

$$|c_c(t)|^2 = \frac{\Gamma_0/2\pi}{{\Gamma_0}^2/4 + (E-E_r)^2} \left[1 - e^{-i(E-E_r)T} e^{-\Gamma_0 T/2} \right] \tag{4.101}$$

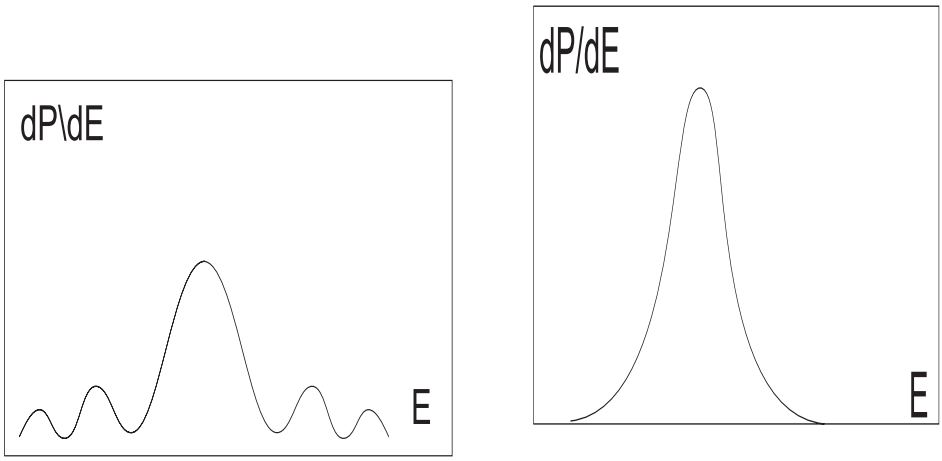
Let us investigate the extreme cases of this result

- $\Gamma_0 T \gg 1$ The time after the decay began is large compared to the natural decay time $1/\Gamma_0$. We obtain a Breit-Wiegner spectrum with line width Γ_0

$$|c_c(t)|^2 = \frac{\Gamma_0/2\pi}{{\Gamma_0}^2/4 + (E - E_r)^2} \tag{4.102}$$

- $\Gamma_0 T \ll 1$ We measure immediately after the decay started. We obtain an oscillating function with maximum atE_r having a width decreasing with T. It's peak increases quadratically.

$$|c_c(t)|^2 = \frac{\Gamma_0}{2\pi}\frac{|1 - e^{i(E-E_r)T}|^2}{(E - E_r)^2} = \frac{\Gamma_0 T^2}{2\pi}\left[\frac{sin(E - E_r)T/2}{(E - E_r)T/2}\right]^2 \tag{4.103}$$



$|c_c(t)|^2$ for $\Gamma_0 T \ll 1$ $|c_c(t)|^2$ for $\Gamma_0 T \gg 1$

Figure 4.8: both

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