Chapter 6. Perturbative Approaches

This chapter discusses several perturbative approaches to problems of quantum mechanics, and their simplest but important applications starting with the fine structure of atomic energy levels, and the effects of external dc and ac electric and magnetic fields on these levels. It continues with a discussion of quantum transitions to continuous spectrum and the Golden Rule of quantum mechanics, which naturally brings us to the issue of open quantum systems – to be discussed in the next chapter.

6.1. Time-independent perturbations

Unfortunately, only a few problems of quantum mechanics may be solved exactly in an analytical form. Actually, in the previous chapters we have solved a substantial part of such problems for a single particle, while for multiparticle systems, the exactly solvable cases are even more rare. However, most practical problems of physics feature a certain small parameter, and this smallness may be exploited by various approximate analytical methods giving *asymptotically correct* results – i.e. the results whose error tends to zero at the reduction of the small parameter(s). Earlier in the course, we explored one of them, the WKB approximation, which is adequate for a particle moving through a soft potential profile. In this chapter, we will discuss other techniques that are more suitable for other cases. The historical name for these techniques is *the perturbation theory*, but it is fairer to speak about *perturbative approaches* because they are substantially different for different situations.

The simplest version of the perturbation theory addresses the problem of stationary states and energy levels of systems described by time-independent Hamiltonians of the type

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}, \tag{6.1}$$

where the operator $\hat{H}^{(1)}$, describing the system's "perturbation", is relatively small – in the sense that its addition to the unperturbed operator $\hat{H}^{(0)}$ results in a relatively small change of the eigenenergies E_n and the corresponding eigenstates of the system. A typical problem of this type is the 1D *weakly anharmonic oscillator* (Fig. 1), described by the Hamiltonian (1) with

Weakly anharmonic oscillator

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \frac{m\omega_0^2 \hat{x}^2}{2}, \qquad \hat{H}^{(1)} = \alpha\hat{x}^3 + \beta\hat{x}^4 + ... \tag{6.2}$$

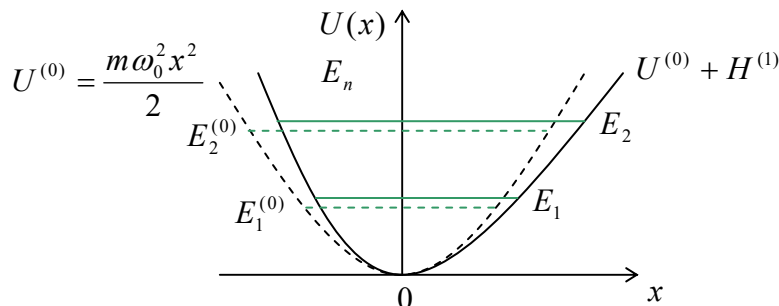with sufficiently small coefficients α, β, ….

Fig. 6.1. The simplest application of the perturbation theory: a weakly anharmonic 1D oscillator. (Dashed lines characterize the unperturbed harmonic oscillator.)

I will use this system as our first example, but let me start by describing the perturbative approach to the general time-independent Hamiltonian (1). In the bra-ket formalism, the eigenproblem (4.68) for the perturbed Hamiltonian, i.e. the stationary Schrödinger equation of the system, is

$$\left(\hat{H}^{(0)} + \hat{H}^{(1)}\right)|n\rangle = E_n|n\rangle. \tag{6.3}$$

Let the eigenstates and eigenvalues of the unperturbed Hamiltonian, which satisfy the equation

$$\hat{H}^{(0)}\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle, \tag{6.4}$$

be considered as known. In this case, the solution of problem (3) means finding, first, its perturbed eigenvalues E_n and, second, the coefficients $\langle n'^{(0)}|n\rangle$ of the expansion of the perturbed state's vectors $|n\rangle$ in the following series over the unperturbed ones, $|n'^{(0)}\rangle$:

$$|n\rangle = \sum_{n'}\left|n'^{(0)}\right\rangle\left\langle n'^{(0)}\,\middle|\,n\right\rangle. \tag{6.5}$$

Let us plug Eq. (5), with the summation index n' replaced with n'' (just to have a more compact notation in our forthcoming result), into both sides of Eq. (3):

$$\sum_{n''}\left\langle n''^{(0)}\,\middle|\,n\right\rangle\hat{H}^{(0)}\left|n''^{(0)}\right\rangle + \sum_{n''}\left\langle n''^{(0)}\,\middle|\,n\right\rangle\hat{H}^{(1)}\left|n''^{(0)}\right\rangle = \sum_{n''}\left\langle n''^{(0)}\,\middle|\,n\right\rangle E_n\left|n''^{(0)}\right\rangle. \tag{6.6}$$

and then inner-multiply all terms by an arbitrary unperturbed bra-vector $\langle n'^{(0)}|$ of the system. Assuming that the unperturbed eigenstates are orthonormal, $\langle n'^{(0)}|n''^{(0)}\rangle = \delta_{n'n''}$, and using Eq. (4) in the first term on the left-hand side, we get the following system of linear equations

$$\sum_{n''}\left\langle n''^{(0)}\,\middle|\,n\right\rangle H_{n'n''}^{(1)} = \left\langle n'^{(0)}\,\middle|\,n\right\rangle\left(E_n - E_{n'}^{(0)}\right), \tag{6.7}$$

where the matrix elements of the perturbation are calculated, by definition, in the *unperturbed* brackets:

$$\boxed{H_{n'n''}^{(1)} \equiv \left\langle n'^{(0)}\,\middle|\,\hat{H}^{(1)}\,\middle|\,n''^{(0)}\right\rangle.} \tag{6.8}$$

Perturbation's matrix elements

The linear equation system (7) is still exact,[1] and is frequently used for numerical calculations. (Since the matrix coefficients (8) typically decrease when n' and/or n'' become sufficiently large, the sum on the left-hand side of Eq. (7) may usually be truncated, still giving an acceptable accuracy of the solution.) To get analytical results, we need to make approximations. In the simple perturbation theory we are discussing now, this is achieved by the expansion of both the eigenenergies and the expansion coefficients into the Taylor series in a certain small parameter μ of the problem:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}..., \tag{6.9}$$

$$\left\langle n'^{(0)}\,\middle|\,n\right\rangle = \left\langle n'^{(0)}\,\middle|\,n\right\rangle^{(0)} + \left\langle n'^{(0)}\,\middle|\,n\right\rangle^{(1)} + \left\langle n''^{(0)}\,\middle|\,n\right\rangle^{(2)}..., \tag{6.10}$$

where

$$E_n^{(k)} \propto \left\langle n'^{(0)}\,\middle|\,n\right\rangle^{(k)} \propto \mu^k. \tag{6.11}$$

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[1] Please note the similarity of Eq. (7) to Eq. (2.215) of the 1D band theory. Indeed, the latter equation is just a particular form of Eq. (7) for the 1D wave mechanics, with a specific (periodic) potential $U(x)$ considered as the perturbation Hamiltonian. Moreover, the whole approximate treatment of the weak-potential limit in Sec. 2.7 was essentially a particular case of the perturbation theory we are discussing now (in its 1st order).

In order to explore the 1st-order approximation, which ignores all terms $O(\mu^2)$ and higher, let us plug only the two first terms of the expansions (9) and (10) into the basic equation (7):

$$\sum_{n''} H^{(1)}_{n'n''}\left(\delta_{n''n} + \left\langle n''^{(0)}\big|n\right\rangle^{(1)}\right) = \left(\delta_{n'n} + \left\langle n'^{(0)}\big|n\right\rangle^{(1)}\right)\left(E^{(0)}_n + E^{(1)}_n - E^{(0)}_{n'}\right). \qquad (6.12)$$

Now let us open the parentheses, and disregard all the remaining terms $O(\mu^2)$. The result is

$$H^{(1)}_{n'n} = \delta_{n'n}E^{(1)}_n + \left\langle n'^{(0)}\big|n\right\rangle^{(1)}(E^{(0)}_n - E^{(0)}_{n'}), \qquad (6.13)$$

This relation is valid for any choice of the indices n and n'; let us start from the case $n = n'$, immediately getting a very simple (and practically, the most important!) result:

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Energy: 1st-order correction

$$E^{(1)}_n = H^{(1)}_{nn} \equiv \left\langle n^{(0)}\big|\hat{H}^{(1)}\big|n^{(0)}\right\rangle. \qquad (6.14)$$

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For example, let us see what this result gives for two first perturbation terms in the weakly anharmonic oscillator (2):

$$E^{(1)}_n = \alpha\left\langle n^{(0)}\big|\hat{x}^3\big|n^{(0)}\right\rangle + \beta\left\langle n^{(0)}\big|\hat{x}^4\big|n^{(0)}\right\rangle. \qquad (6.15)$$

As the reader knows (or should know :-) from the solution of Problem 5.12, the first bracket equals zero, while the second one yields

$$E^{(1)}_n = \frac{3}{4}\beta x^4_0\left(2n^2 + 2n + 1\right). \qquad (6.16)$$

Naturally, there should be some non-vanishing contribution to the energies from the (typically, larger) perturbation proportional to α, so for its calculation, we need to explore the 2nd order of the theory. However, before doing that, let us complete our discussion of its 1st order.

For $n' \neq n$, Eq. (13) may be used to calculate the eigenstates rather than the eigenvalues:

$$\left\langle n'^{(0)}\big|n\right\rangle^{(1)} = \frac{H^{(1)}_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}}, \qquad \text{for } n' \neq n. \qquad (6.17)$$

This means that the eigenket's expansion (5), in the 1st order, may be represented as

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States: 1st-order result

$$\big|n^{(1)}\big\rangle = C\big|n^{(0)}\big\rangle + \sum_{n'\neq n}\frac{H^{(1)}_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}}\big|n'^{(0)}\big\rangle. \qquad (6.18)$$

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The coefficient $C \equiv \langle n^{(0)}|n^{(1)}\rangle$ cannot be found from Eq. (17); however, requiring the final state n to be normalized, we see that other terms may provide only corrections $O(\mu^2)$, so in the 1st order we should take $C = 1$. The most important feature of Eq. (18) is its denominators: the closer the unperturbed eigenenergies of two states, the larger their mutual "interaction" due to the perturbation.

This feature also affects the 1st-order approximation's validity condition, which may be quantified using Eq. (17): the magnitudes of the brackets it describes have to be much less than the unperturbed bracket $\langle n|n\rangle^{(0)} = 1$, so all elements of the perturbation matrix have to be much less than the difference between the corresponding unperturbed energies. For the anharmonic oscillator's energy corrections (16), this requirement is reduced to $E^{(1)}_n \ll \hbar\omega_0$.

Now we are ready to go after the 2nd-order approximation to Eq. (7). Let us focus on the case n' = n, because as we already know, only this term will give us a correction to the eigenenergies. Moreover, since the left-hand side of Eq. (7) already has a small factor $H^{(1)}_{n'n''} \propto \mu$, the bracket coefficients in that part may be taken from the 1st-order result (17). As a result, we get

$$E_n^{(2)} = \sum_{n''} \left\langle n''^{(0)} \left| n \right\rangle^{(1)} H_{nn''}^{(1)} = \sum_{n'' \neq n} \frac{H_{n''n}^{(1)} H_{nn''}^{(1)}}{E_n^{(0)} - E_{n''}^{(0)}}. \qquad (6.19)$$

Since $\hat{H}^{(1)}$ has to be Hermitian, we may rewrite this expression as

$$E_n^{(2)} = \sum_{n' \neq n} \frac{\left| H_{n'n}^{(1)} \right|^2}{E_n^{(0)} - E_{n'}^{(0)}} \equiv \sum_{n' \neq n} \frac{\left| \left\langle n'^{(0)} \left| \hat{H}^{(1)} \right| n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_{n'}^{(0)}}. \qquad (6.20)$$

Energy:
2nd-order
correction

This is the much-celebrated 2nd-order perturbation result, which frequently (in sufficiently symmetric problems) is the *first non-vanishing* correction to the state energy – for example, from the cubic term (proportional to α) in our weakly anharmonic oscillator problem (2). To calculate the corresponding correction, we may use another result of the solution of Problem 5.12:

$$\left\langle n' \left| \hat{x}^3 \right| n \right\rangle = \left(\frac{x_0}{\sqrt{2}} \right)^3$$
$$\times \left\{ [n(n-1)(n-2)]^{1/2} \delta_{n',n-3} + 3n^{3/2} \delta_{n',n-1} + 3(n+1)^{3/2} \delta_{n',n+1} + [(n+1)(n+2)(n+3)]^{1/2} \delta_{n',n+3} \right\}. \qquad (6.21)$$

So, according to Eq. (20), we need to calculate

$$E_n^{(2)} = \alpha^2 \left(\frac{x_0}{\sqrt{2}} \right)^6$$
$$\times \sum_{n' \neq n} \frac{\left\{ [n(n-1)(n-2)]^{1/2} \delta_{n',n-3} + 3n^{3/2} \delta_{n',n-1} + 3(n+1)^{3/2} \delta_{n',n+1} + [(n+1)(n+2)(n+3)]^{1/2} \delta_{n',n+3} \right\}^2}{\hbar \omega_0 (n - n')}. \qquad (6.22)$$

The summation is not as cumbersome as may look because, at the curly bracket's squaring, all mixed products are proportional to the products of different Kronecker deltas and hence vanish, so we need to sum up only the squares of each term, finally getting

$$E_n^{(2)} = -\frac{15}{4} \frac{\alpha^2 x_0^6}{\hbar \omega_0} \left(n^2 + n + \frac{11}{30} \right). \qquad (6.23)$$

This formula shows that all 2nd-order energy level corrections are negative, regardless of the sign of α.[2] On the contrary, the 1st-order correction $E_n^{(1)}$ given by Eq. (16), does depend on the sign of β, so the net correction, $E_n^{(1)} + E_n^{(2)}$, may be of any sign.

The results (18) and (20) are clearly inapplicable to the degenerate case where, in the absence of perturbation, several states correspond to the same energy level, because of the divergence of their denominators.[3] This divergence hints that in this case, the largest effect of the perturbation is the

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[2] Note that this is correct for the ground-state energy correction $E_g^{(2)}$ of *any* system, because for this state, the denominators of all terms of the sum (20) are negative, while their numerators are always non-negative.

[3] This is exactly the reason why this simple perturbation approach runs into serious problems for systems with a continuous spectrum, and other techniques (such as the WKB approximation) are often necessary.

degeneracy lifting, e.g., some splitting of the initially degenerate energy level $E^{(0)}$ (Fig. 2), and that for the analysis of this case, we can, in the first approximation, ignore the effect of all other energy levels. (A more detailed analysis shows that this is indeed the case until the level splitting becomes comparable with the distance to other energy levels.)
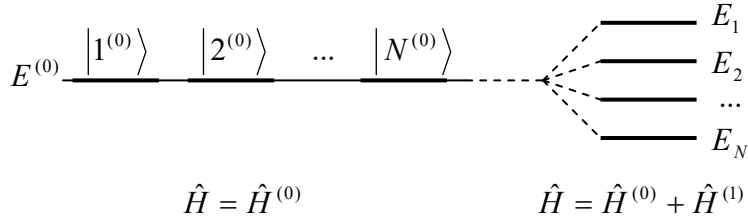

Fig. 5.2. Lifting the energy level degeneracy by a perturbation (schematically).

Limiting the summation in Eq. (7) to a group of N degenerate states with equal $E_{n'}^{(0)} \equiv E^{(0)}$, we reduce it to

$$\sum_{n''=1}^{N} \langle n''^{(0)} | n \rangle H_{n'n''}^{(1)} = \langle n'^{(0)} | n \rangle (E_n - E^{(0)}), \qquad (6.24)$$

where now the indices n' and n'' number the N states of the group.[4] For $n = n'$, Eq. (24) may be rewritten as

$$\sum_{n''=1}^{N} \left(H_{n'n''}^{(1)} - E_{n''}^{(1)} \delta_{n'n''} \right) \langle n''^{(0)} | n' \rangle = 0, \quad \text{where } E_n^{(1)} \equiv E_n - E^{(0)}. \qquad (6.25)$$

For each $n' = 1, 2, \ldots N$, this is a system of N linear, homogenous equations (with N terms each) for N unknown coefficients $\langle n''^{(0)} | n' \rangle$. In this problem, we may readily recognize the problem of diagonalization of the perturbation matrix $H^{(1)}$ – cf. Sec. 4.4 and in particular Eq. (4.101). As in the general case, the condition of self-consistency of the system is:

$$\begin{vmatrix} H_{11}^{(1)} - E_n^{(1)} & H_{12}^{(1)} & \cdots \\ H_{21}^{(1)} & H_{22}^{(1)} - E_n^{(1)} & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} = 0, \qquad (6.26)$$

where now the index n numbers the N roots of this equation, in arbitrary order. According to the definition (25) of $E_n^{(1)}$, the resulting N energy levels E_n may be found as $E^{(0)} + E_n^{(1)}$. If the perturbation matrix is diagonal in the chosen basis $n^{(0)}$, the result is extremely simple,

$$E_n - E^{(0)} \equiv E_n^{(1)} = H_{nn}^{(1)}, \qquad (6.27)$$

and formally coincides with Eq. (14) for the non-degenerate case, but now it may give a different result for each of N previously degenerate states n.

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[4] Note that here the choice of the basis is to some extent arbitrary because due to the linearity of equations of quantum mechanics, any linear combination of the states $n''^{(0)}$ is also an eigenstate of the unperturbed Hamiltonian. However, for using Eq. (25), these combinations have to be orthonormal, as was supposed in the derivation of Eq. (7).

Now let us see what this general theory gives for several important examples. First of all, let us consider a system with just two degenerate states with energy sufficiently far from all other levels. Then, in the basis of these two degenerate states, the most general perturbation matrix is

$$\mathrm{H}^{(1)} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{6.28}$$

This matrix coincides with the general matrix (5.2) of a two-level system. Hence, we come to the very important conclusion: for a weak perturbation, all properties of any double-degenerate system are identical to those of the genuine two-level systems, which were the subject of numerous discussions in Chapter 4 and again in Sec. 5.1. In particular, its eigenenergies are given by Eq. (5.6), and may be described by the level-anticrossing diagram shown in Fig. 5.1.

6.2. The linear Stark effect

As a more involved example of the level degeneracy lifting by a perturbation, let us discuss the *Stark effect*[5] – the atomic level splitting by an external electric field. Let us study this effect, in the linear approximation, for a hydrogen-like atom/ion.[6] Taking the direction of the external electric field $\mathscr{E}$ (which is practically always uniform on the atomic scale) for the z-axis, the perturbation may be represented by the following Hamiltonian:

$$\hat{H}^{(1)} = -F\hat{z} = -q\mathscr{E}\hat{z} = -q\mathscr{E}r\cos\theta . \tag{6.29}$$

(In the last form, the operator sign is dropped, because we will work in the coordinate representation.)

As you (should :-) remember, energy levels of a hydrogen-like atom/ion depend only on the principal quantum number n – see Eq. (3.201); hence all the states, besides the ground $1s$ state with $n = 1$ and $l = m = 0$, have some orbital degeneracy, which grows rapidly with n. Let us consider the lowest degenerate level with $n = 2$. Since, according to Eq. (3.203), $0 \le l \le n - 1$, at this level the orbital quantum number l may equal either 0 (one $2s$ state, with $m = 0$) or 1 (three $2p$ states, with $m = 0, \pm 1$). Due to this 4-fold degeneracy, $\mathrm{H}^{(1)}$ is a 4×4 matrix with 16 elements:

$$\mathrm{H}^{(1)} = \begin{matrix} & \overbrace{l=0}^{} \quad \overbrace{l=1}^{} \\ \underbrace{m=0}_{} \; \underbrace{m=0}_{} \; \underbrace{m=+1}_{} \; \underbrace{m=-1}_{} \\ \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} \begin{matrix} m=0, & l=0, \\ m=0, \\ m=+1, \\ m=-1, \end{matrix} \left. \begin{matrix} \\ \\ \end{matrix} \right\} l=1. \end{matrix} \tag{6.30}$$

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[5] This effect was discovered experimentally in 1913 by Johannes Stark and independently by Antonio Lo Surdo, so it is sometimes (and more fairly) called the "Stark – Lo Surdo effect". Sometimes this name is used with the qualifier "dc" to distinguish it from the *ac Stark* effect – the energy level shift under the effect of an ac field – see Sec. 5 below.

[6] An analysis of the *quadratic Stark effect* for the ground-state energy in the same system, changing with the field only as $\mathscr{E}^2$, is left for the reader's exercise.

However, there is no need to be scared. First, due to the Hermitian nature of the operator, only 10 of these 16 matrix elements (4 diagonal and 6 off-diagonal ones) may be substantially different from each other. Moreover, due to the high symmetry of the problem, there are a lot of zeros even among these elements. Indeed, let us have a look at the angular components Y_l^m of the corresponding wavefunctions, with $l = 0$ and $l = 1$, described by Eqs. (3.174)-(3.175). For the states with $m = \pm 1$, the azimuthal parts of wavefunctions are proportional to $\exp\{\pm i\varphi\}$; hence the off-diagonal elements H_{34} and H_{43} of the matrix (30), relating these functions, are proportional to

$$\oint d\Omega \, Y_1^{\pm *} \hat{H}^{(1)} Y_1^{\mp} \propto \int_0^{2\pi} d\varphi \left(e^{\pm i\varphi} \right)^* \left(e^{\mp i\varphi} \right) = 0. \tag{6.31}$$

The azimuthal-angle symmetry also kills the off-diagonal elements H_{13}, H_{14}, H_{23}, H_{24} (and hence their complex conjugates H_{31}, H_{41}, H_{32}, and H_{42}), because they relate states with $m = 0$ and $m = \pm 1$, and hence are proportional to

$$\oint d\Omega \, Y_1^{0 *} \hat{H}^{(1)} Y_1^{\pm 1} \propto \int_0^{2\pi} d\varphi \, e^{\pm i\varphi} = 0. \tag{6.32}$$

For the diagonal matrix elements H_{33} and H_{44}, corresponding to $l = 1$ and $m = \pm 1$, the azimuthal-angle integrals do not vanish, but since the corresponding spherical harmonics depend on the polar angle as $\sin\theta$, these elements are proportional to

$$\oint d\Omega \, Y_1^{\pm 1 *} \hat{H}^{(1)} Y_1^{\pm 1} \propto \int_0^\pi \sin\theta d\theta \, \sin\theta \cos\theta \sin\theta = \int_{-1}^{+1} \cos\theta \left(1 - \cos^2\theta \right) d(\cos\theta), \tag{6.33}$$

and hence are equal to zero – as any limit-symmetric integral of an odd function. Finally, for the states 2s and 2p with $m = 0$, the diagonal elements H_{11} and H_{22} are also killed by the polar-angle integration:

$$\oint d\Omega \, Y_0^{0 *} \hat{H}^{(1)} Y_0^0 \propto \int_0^\pi \sin\theta d\theta \cos\theta = \int_{-1}^1 \cos\theta \, d(\cos\theta) = 0 , \tag{6.34}$$

$$\oint d\Omega \, Y_0^{1 *} \hat{H}^{(1)} Y_0^1 \propto \int_0^\pi \sin\theta d\theta \cos^3\theta = \int_{-1}^{+1} \cos^3\theta \, d(\cos\theta) = 0. \tag{6.35}$$

Hence, the only non-zero elements of the matrix (30) are two off-diagonal elements H_{12} and H_{21}, which relate two states with the same $m = 0$, but different $l = \{0, 1\}$, because they are proportional to

$$\oint d\Omega \, Y_0^{0 *} \cos\theta \, Y_1^0 = \frac{\sqrt{3}}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \cos^2\theta = \frac{1}{\sqrt{3}} \neq 0. \tag{6.36}$$

What remains is to use Eqs. (3.209) for the radial parts of these functions to complete the calculation of those two matrix elements:

$$H_{12} = H_{21} = -\frac{q\mathcal{E}}{\sqrt{3}} \int_0^\infty r^2 dr \mathcal{R}_{2,0}(r) r \mathcal{R}_{2,1}(r). \tag{6.37}$$

Due to the additive structure of the function $\mathcal{R}_{2,0}(r)$, the integral falls into a sum of two table integrals, both of the type MA Eq. (6.7d), finally giving

$$H_{12} = H_{21} = 3q\mathcal{E}r_0, \tag{6.38}$$

where r_0 is the spatial scale (3.192); for the hydrogen atom, it is just the Bohr radius r_B – see Eq. (1.10).

Thus, the perturbation matrix (30) is reduced to

$$H^{(1)} = \begin{pmatrix} 0 & 3q\mathscr{E}r_0 & 0 & 0 \\ 3q\mathscr{E}r_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{6.39}$$

so the condition (26) of self-consistency of the system (25),

$$\begin{vmatrix} -E_2^{(1)} & 3q\mathscr{E}r_0 & 0 & 0 \\ 3q\mathscr{E}r_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0, \tag{6.40}$$

gives a very simple characteristic equation

$$\left(E_2^{(1)}\right)^2 \left[\left(E_2^{(1)}\right)^2 - \left(3q\mathscr{E}r_0\right)^2\right] = 0. \tag{6.41}$$

with four roots:

$$\left(E_2^{(1)}\right)_{1,2} = 0, \qquad \left(E_2^{(1)}\right)_{3,4} = \pm 3q\mathscr{E}r_0. \tag{6.42}$$

so the degeneracy is only partly lifted – see the levels in Fig. 3.
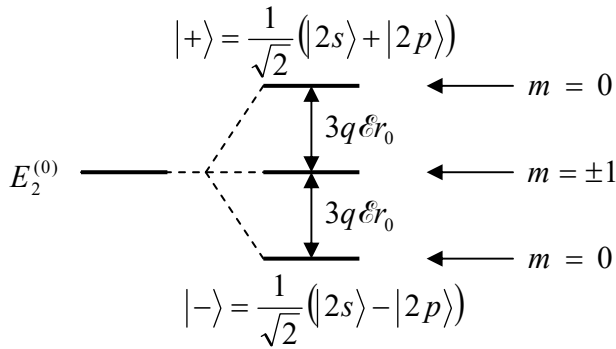

Fig. 6.3. The linear Stark effect for the level $n = 2$ of a hydrogen-like atom.

Generally, in order to understand the nature of states corresponding to these levels, we should return to Eq. (25) with each calculated value of $E_2^{(1)}$, and find the corresponding expansion coefficients $\langle n''^{(0)}|n'\rangle$ that describe the perturbed states. However, in our simple case, the outcome of this procedure is clear in advance. Indeed, since the states with $\{l = 1, m = \pm 1\}$ are not affected by the perturbation at all (in the linear approximation in the electric field), their degeneracy is not lifted, and energy is not affected – see the middle line in Fig. 3. On the other hand, the partial perturbation matrix connecting the states $2s$ and $2p$, i.e. the top left 2×2 part of the full matrix (39), is proportional to the Pauli matrix σ_x, and we already know the result of its diagonalization – see Eqs. (4.113)-(4.114). This means that the upper and lower split levels correspond to very simple linear combinations of the previously degenerate states with $m = 0$,

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|2s\rangle \pm |2p\rangle\right). \tag{6.43}$$

Finally, let us estimate the magnitude of the linear Stark effect for a hydrogen atom. For a very high dc electric field of $\mathscr{E} = 3\times10^6$ V/m,[7] $|q| = e \approx 1.6\times10^{-19}$ C, and $r_0 = r_B \approx 0.5\times10^{-10}$ m, we get a level splitting of $3q\mathscr{E}r_0 \approx 0.8\times10^{-22}$ J ≈ 0.5 meV. This number is much lower than the unperturbed energy of the level, $E_2 = -E_H/(2\times2^2) \approx -3.4$ eV, so the perturbative result is quite applicable. On the other hand, the calculated splitting is much larger than the resolution limit imposed by the line's natural width ($\sim10^{-7}\,E_2$, see Chapter 9), so the effect is quite observable even in substantially lower electric fields. Note, however, that our simple results are quantitatively correct only when the Stark splitting (42) is much larger than the fine-structure splitting of the same level in the absence of the field– see the next section.

6.3. Fine structure of atomic levels

Now let us use the same perturbation theory to analyze, also for the simplest case of a hydrogen-like atom/ion, the so-called *fine structure* of atomic levels – their degeneracy lifting even in the absence of external fields. Since the effective speed v of the electron motion in atoms is much smaller than the speed of light c, the fine structure may be analyzed as a sum of two independent relativistic effects. To analyze the first of them, let us expand the well-known classical relativistic expression[8] for the kinetic energy $T = E - mc^2$ of a free particle with the rest mass m,[9]

$$T = \left(m^2c^4 + p^2c^2\right)^{1/2} - mc^2 \equiv mc^2\left[\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} - 1\right], \tag{6.44}$$

into the Taylor series in the small ratio $(p/mc)^2 \approx (v/c)^2$:

$$T = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + ... - 1\right] \equiv \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + ..., \tag{6.45}$$

and drop all the terms besides the two spelled-out ones. Of them, the first term is non-relativistic, while the second one represents the main relativistic correction to T.

Following the correspondence principle, the quantum-mechanical problem in this approximation may be described by Eq. (1) with the unperturbed Hamiltonian

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \hat{U}(r), \qquad \hat{U}(r) = -\frac{C}{r}, \tag{6.46}$$

(whose eigenstates and eigenenergies were discussed in Sec. 3.5) and the kinetic-relativistic perturbation

Kinetic-relativistic perturbation

$$\hat{H}^{(1)} = -\frac{\hat{p}^4}{8m^3c^2} \equiv -\frac{1}{2mc^2}\left(\frac{\hat{p}^2}{2m}\right)^2. \tag{6.47}$$

Using Eq. (46), we may rewrite the last formula as

---

[7] This value approximately corresponds to the threshold of electric breakdown in the air at ambient conditions, due to the impact ionization. As a result, experiments with higher dc fields are rather difficult.
[8] See, e.g., EM Eq. (9.78).
[9] This fancy font is used, as in Secs. 3.5-3.8, to distinguish the mass m from the magnetic quantum number m.

$$\hat{H}^{(1)} = -\frac{1}{2mc^2}\left(\hat{H}^{(0)} - \hat{U}(r)\right)^2, \tag{6.48}$$

so its matrix elements participating in the characteristic equation (25) for a given degenerate energy level (3.201), i.e. a given principal quantum number n, are

$$\left\langle nlm \middle| \hat{H}^{(1)} \middle| nl'm' \right\rangle = -\frac{1}{2mc^2}\left\langle nlm \middle| \left(\hat{H}^{(0)} - \hat{U}(r)\right)\left(\hat{H}^{(0)} - \hat{U}(r)\right)\middle| nl'm' \right\rangle, \tag{6.49}$$

where the bra- and ket-vectors describe the unperturbed eigenstates, whose eigenfunctions (in the coordinate representation) are given by Eq. (3.200): $\psi_{n,l,m} = \mathcal{R}_{n,l}(r)Y_l^m(\theta,\varphi)$.

It is straightforward (and hence left for the reader's exercise) to prove that all off-diagonal elements of the set (49) are equal to 0. Thus we may use Eq. (27) for each set of the quantum numbers $\{n, l, m\}$:

$$E_{n,l,m}^{(1)} \equiv E_{n,l,m} - E_n^{(0)} = \left\langle nlm \middle| \hat{H}^{(1)} \middle| nlm \right\rangle = -\frac{1}{2mc^2}\left\langle \left(\hat{H}^{(0)} - \hat{U}(r)\right)^2 \right\rangle_{n,l,m}$$

$$= -\frac{1}{2mc^2}\left(E_n^2 - 2E_n\langle\hat{U}\rangle_{n,l} + \langle\hat{U}^2\rangle_{n,l}\right) = -\frac{1}{2mc^2}\left(\frac{E_0^2}{4n^4} - \frac{E_0}{n^2}C\left\langle\frac{1}{r}\right\rangle_{n,l} + C^2\left\langle\frac{1}{r^2}\right\rangle_{n,l}\right), \tag{6.50}$$

where the index m has been dropped, because the radial wavefunctions $\mathcal{R}_{n,l}(r)$, which affect these expectation values, do not depend on that quantum number. Now using Eqs. (3.191), (3.201) and the first two of Eqs. (3.211), we finally get

$$E_{n,l}^{(1)} = -\frac{mC^2}{2\hbar^2 c^2 n^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right) \equiv -\frac{2E_n^2}{mc^2}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right). \tag{6.51}$$

Kinetic-relativistic energy correction

Let us discuss this result. First of all, its last form confirms that the correction (51) is indeed much smaller than the unperturbed energy E_n (and hence the perturbation theory is valid) if the latter is much smaller than the relativistic rest energy mc^2 of the particle – as it is for the hydrogen atom. Next, since in the Bohr problem's solution, $n \geq l + 1$, the first fraction in the parentheses of Eq. (51) is always larger than 1, and hence than ¾, so the kinetic relativistic correction to energy is negative for all n and l. (Actually, this fact could be predicted already from Eq. (47), which shows that the perturbation's Hamiltonian is a negatively defined form.) Finally, for a fixed principal number n, the negative correction's magnitude decreases with the growth of l. This fact may be interpreted using the second of Eqs. (3.211): the larger is l (at fixed n), the larger is the particle's effective distance from the center, and hence the smaller is its effective velocity, i.e. the smaller is the magnitude of the quantum-mechanical average of the negative relativistic correction (47) to the kinetic energy.

The result (51) is valid for the Coulomb interaction $U(r) = -C/r$ of any physical nature. However, if we speak specifically about hydrogen-like atoms/ions, there is also another relativistic correction to energy, due to the so-called *spin-orbit interaction* (alternatively called the "spin-orbit coupling"). Its physics may be understood from the following semi-quantitative classical reasoning: from the "the point of view" of an electron rotating about the nucleus at distance r with velocity $\mathbf{v}$, it is the nucleus, of the electric charge Ze, that rotates about the electron with the velocity $(-\mathbf{v})$ and hence the time period $\mathcal{T} = 2\pi r/v$. From the point of view of magnetostatics, such circular motion of the electric charge $Q = Ze$, is

equivalent to a circular dc electric current $I = Q/\mathcal{T} = (Ze)(v/2\pi r)$. At the electron's location, i.e. in the center of the current loop, it creates the magnetic field with the following magnitude:[10]

$$\mathscr{B}_a = \frac{\mu_0}{2r}I = \frac{\mu_0}{2r}\frac{Zev}{2\pi r} \equiv \frac{\mu_0 Zev}{4\pi r^2}. \tag{6.52}$$

The field's direction $\mathbf{n}$ is perpendicular to the apparent plane of the nucleus' rotation (i.e. that of the real rotation of the electron), and hence its vector may be readily expressed via the similarly directed vector $\mathbf{L} = m_e v r \mathbf{n}$ of the electron's angular (orbital) momentum:

$$\mathscr{B}_a = \frac{\mu_0 Zev}{4\pi r^2}\mathbf{n} \equiv \frac{\mu_0 Ze}{4\pi r^3 m_e}m_e v r \mathbf{n} \equiv \frac{\mu_0 Ze}{4\pi r^3 m_e}\mathbf{L} \equiv \frac{Ze}{4\pi\varepsilon_0 r^3 m_e c^2}\mathbf{L}, \tag{6.53}$$

where the last step used the basic relation between the SI-unit constants: $\mu_0 \equiv 1/c^2\varepsilon_0$.

A more careful (but still classical) analysis of the problem[11] brings both good and bad news. The bad news is that the result (53) is wrong by the so-called *Thomas factor* of two even for the circular motion, because the electron moves with acceleration, and the reference frame bound to it cannot be inertial (as was implied in the above reasoning), so the effective magnetic field felt by the electron is actually

$$\mathscr{B} = \frac{Ze}{8\pi\varepsilon_0 r^3 m_e c^2}\mathbf{L}. \tag{6.54}$$

The good news is that this result is valid not only for circular but an arbitrary orbital motion in the Coulomb field $U(r)$. Hence from the discussion in Sec. 4.1 and Sec. 4.4 we may expect that the quantum-mechanical description of the interaction between this effective magnetic field and the electron's spin moment (4.115) is given by the following perturbation Hamiltonian[12]

$$\hat{H}^{(1)} = -\hat{\mathbf{m}}\cdot\hat{\mathscr{B}} = -\gamma_e\hat{\mathbf{S}}\cdot\left(\frac{Ze}{8\pi\varepsilon_0 r^3 m_e c^2}\hat{\mathbf{L}}\right) \equiv \frac{1}{2m_e^2 c^2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r^3}\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}, \tag{6.55}$$

where at spelling out the electron's gyromagnetic ratio $\gamma_e \equiv -g_e e/2m_e$, the small correction to the value $g_e = 2$ of the electron's g-factor (see Sec. 4.4) is ignored, because Eq. (55) is already a small correction. This expectation is confirmed by the fully-relativistic Dirac theory, to be discussed in Sec. 9.7 below: it yields, for an arbitrary central potential $U(r)$, the following spin-orbit coupling Hamiltonian:

Spin-
orbit
coupling

$$\boxed{\hat{H}^{(1)} = \frac{1}{2m_e^2 c^2}\frac{1}{r}\frac{dU(r)}{dr}\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}.} \tag{6.56}$$

For the Coulomb potential $U(r) = -Ze^2/4\pi\varepsilon_0 r$, this formula is reduced to Eq. (55).

---

[10] See, e.g., EM Sec. 5.1, in particular, Eq. (5.24). Note that such an effective magnetic field is induced by any motion of electrons, in particular that in solids, leading to a variety of spin-orbit effects there – see, e.g., a concise review by R. Winkler *et al.*, in B. Kramer (ed.), *Advances in Solid State Physics* **41**, 211 (2001).

[11] It was carried out first by Llewellyn Thomas in 1926; for a simple review see, e.g., R. Harr and L. Curtis, *Am. J. Phys.* **55**, 1044 (1987).

[12] In the Gaussian units, Eq. (55) is valid without the factor $4\pi\varepsilon_0$ in the denominator; while Eq. (56), "as is".

As we already know from the discussion in Sec. 5.7, the angular factor of this Hamiltonian commutes with all the operators of the coupled-representation group (inside the blue line in Fig. 5.12): $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_z$, and hence is diagonal in the coupled-representation basis with definite quantum numbers l, j, and m_j (and of course $s = \frac{1}{2}$). Hence, using Eq. (5.181) to rewrite Eq. (56) as

$$\hat{H}^{(1)} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{r^3} \frac{1}{2} \left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right), \tag{6.57}$$

we may again use Eq. (27) for each set $\{s, l, j, m_j\}$, with common n:

$$E_{n,j,l}^{(1)} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n,l} \frac{1}{2} \left\langle \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right\rangle_{j,s}, \tag{6.58}$$

where the indices irrelevant for each particular factor have been dropped. Now using the last of Eqs. (3.211), and similar expressions (5.169), (5.175), and (5.177) for eigenvalues of the involved operators, we get an explicit expression for the spin-orbit corrections[13]

$$E_{n,j,l}^{(1)} = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{\hbar^2}{2r_0^3} \frac{j(j+1) - l(l+1) - \frac{3}{4}}{n^3 l(l+\frac{1}{2})(l+1)} \equiv \frac{E_n^2}{m_e c^2} n \frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)}, \tag{6.59}$$

<div style="text-align:right">Spin-orbit energy correction</div>

with l and j related by Eq. (5.189): $j = l \pm \frac{1}{2}$.

The last form of its result shows clearly that this correction has the same magnitude scale as the kinetic correction (51).[14] In the 1st order of the perturbation theory, they may be just added (with $m = m_e$), giving a surprisingly simple formula for the net fine structure of the nth energy level:

$$E_{\text{fine}}^{(1)} = \frac{E_n^2}{2m_e c^2} \left(3 - \frac{4n}{j+\frac{1}{2}} \right). \tag{6.60}$$

<div style="text-align:right">Fine structure of atomic levels</div>

This simplicity, as well as the independence of the result of the orbital quantum number l, will become less surprising when (in Sec. 9.7) we see that this formula follows in one shot from the Dirac theory, in which the Bohr atom's energy spectrum is numbered only with n and j, but not l. Let us recall that for an electron ($s = \frac{1}{2}$), according to Eq. (5.189) with $0 \leq l \leq n - 1$, the quantum number j may take n positive half-integer values, from $\frac{1}{2}$ to $n - \frac{1}{2}$. Hence, Eq. (60) shows that the fine structure of the nth Bohr's energy level has n sub-levels – see Fig. 4.

Please note that according to Eq. (5.175), each of these sub-levels is still $(2j + 1)$-times degenerate in the quantum number m_j. This degeneracy is very natural, because all m-numbers describe the state orientation in a certain direction, while in the absence of an external field, the system is still isotropic. Moreover, on each fine-structure level (besides the highest one with $j = n - \frac{1}{2}$), each of the m_j-states is doubly degenerate in the orbital quantum number $l = j \mp \frac{1}{2}$ – see the labels of l in Fig. 4. (According to Eq. (5.190), each of these states, with fixed j and m_j, may be represented as a linear

---

[13] The factor l in the denominator does not give a divergence at $l = 0$, because in this case $j = s = \frac{1}{2}$, so $j(j + 1) = \frac{3}{4}$, and the numerator turns into 0 as well. A careful analysis of this case (see, e.g., G. Woolgate, *Elementary Atomic Structure*, 2nd ed., Oxford, 1983), including the so-called *Darwin term* not described by Eqs. (51) and (59), shows that the final Eq. (60), which does not include l, is valid even in this case.

[14] This is natural because the magnetic interaction of charged particles is essentially a relativistic effect, of the same order ($\sim v^2/c^2$) as the kinetic correction (47) – see, e.g., EM Sec. 5.1, in particular Eq. (5.3).

combination of two states with adjacent values of l, and hence different electron spin orientations, $m_s = \pm\frac{1}{2}$, weighed with the Clebsch-Gordan coefficients.)
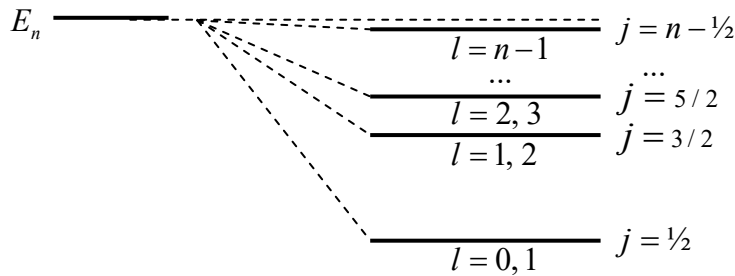

Fig. 6.4. The fine structure of a hydrogen-like atom/ion's level.

These details aside, one may crudely say that the relativistic corrections combined make the total eigenenergy grow with l, contributing to the effect already mentioned in the discussion of the periodic table of elements in Sec. 3.7. The relative scale of this increase may be quantified by the largest deviation from the unperturbed energy E_n, reached for the s-states (with $l = 0$):

$$\frac{\left|E_{\max}^{(1)}\right|}{E_n} = \frac{E_n}{2m_e c^2}(4n-3) \equiv \left(\frac{Ze^2}{4\pi\varepsilon_0 \hbar c}\right)^2 \left(\frac{1}{n} - \frac{3}{4n^2}\right) \equiv Z^2\alpha^2\left(\frac{1}{n} - \frac{3}{4n^2}\right). \tag{6.61}$$

where α is the *fine-structure* ("Sommerfeld's") *constant*,

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}, \tag{6.62}$$

(which was already mentioned in Sec. 4.4), which characterizes the relative strength (or rather weakness) of the electromagnetic effects in quantum mechanics – which in particular makes perturbative quantum electrodynamics possible.[15] These expressions show that the fine-structure splitting is a very small effect ($\sim\alpha^2 \sim 10^{-6}$) for the hydrogen atom, but it rapidly grows (as Z^2) with the nuclear charge (i.e. the atomic number) Z, and becomes rather substantial for the heaviest stable atoms with $Z \sim 10^2$.

6.4. The Zeeman effect

Now, we are ready to review the *Zeeman effect* – the atomic level splitting by an external magnetic field.[16] Using Eq. (3.26), with $q = -e$, for the description of the electron's orbital motion in the field, and the Pauli Hamiltonian (4.163) with $\gamma = -e/m_e$, for the electron spin's interaction with the field, we see that even for a hydrogen-like (i.e. single-electron) atom/ion, neglecting the relativistic effects, the full Hamiltonian is rather involved:

$$\hat{H} = \frac{1}{2m_e}\left(\hat{\mathbf{p}} + e\hat{\mathbf{A}}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{e}{m_e}\boldsymbol{\mathscr{B}} \cdot \hat{\mathbf{S}}. \tag{6.63}$$

---

[15] The expression $\alpha^2 = E_H/m_e c^2$, where E_H is the Hartree energy (1.13), i.e. the scale of the basic energies E_n, is also very revealing.

[16] It was discovered experimentally in 1896 by Pieter Zeeman who, amazingly, was fired from the University of Leiden for unauthorized use of lab equipment for this work – just to receive a Nobel Prize for it in a few years!

There are several simplifications we may make. First, let us assume that the external field is spatial-uniform on the atomic scale (which is a very good approximation for most cases), so we can take its vector potential in an axially symmetric gauge – cf. Eq. (3.132):

$$\mathbf{A} = \frac{1}{2}\boldsymbol{\mathscr{B}} \times \mathbf{r}. \tag{6.64}$$

Second, let us neglect the terms proportional to $\mathscr{B}^2$, which are small in practical magnetic fields of the order of a few teslas.[17] The remaining term in the effective kinetic energy, describing the interaction with the magnetic field, is linear in the momentum operator, so we may repeat the standard classical calculation[18] to reduce it to the product of $\mathscr{B}$ by the orbital magnetic moment's component $m_z = -eL_z/2m_e$ – besides that both m_z and L_z should be understood as operators now. As a result, the Hamiltonian (63) reduces to Eq. (1), $\hat{H}^{(0)} + \hat{H}^{(1)}$, where $\hat{H}^{(0)}$ is that of the atom at $\mathscr{B} = 0$, and

$$\hat{H}^{(1)} = \frac{e\mathscr{B}}{2m_e}\left(\hat{L}_z + 2\hat{S}_z\right) \tag{6.65}$$

Zeeman effect's perturbation

This expression immediately reveals the major complication with the Zeeman effect's analysis. Namely, in comparison with the equal orbital and spin contributions to the total angular momentum (5.170) of the electron, its spin produces a twice larger contribution to the magnetic moment, so the right-hand side of Eq. (65) is *not* proportional to $\hat{J}_z = \hat{L}_z + \hat{S}_z$. As a result, the effect's description is quite simple only in two limits.

If the magnetic field is so *high* that its effects are much stronger than the relativistic (fine-structure) effects discussed in the previous section, we may treat the two terms in Eq. (65) as independent perturbations of different (orbital and spin) degrees of freedom. Since each of the perturbation matrices is diagonal in its own *z*-basis, we can again use Eq. (27) to write

$$E - E^{(0)} = \frac{e\mathscr{B}}{2m_e}\left(\langle n,l,m_l|\hat{L}_z|n,l,m_l\rangle + 2\langle m_s|\hat{S}_z|m_s\rangle\right) = \frac{e\mathscr{B}}{2m_e}\left(\hbar m_l + 2\hbar m_s\right) = \mu_B \mathscr{B}(m_l \pm 1). \tag{6.66}$$

Paschen-Back effect

This result describes the splitting of each $2\times(2l+1)$-degenerate energy level, with certain n and l, into $(2l+3)$ levels (Fig. 5), with the adjacent level distance of $\mu_B\mathscr{B}$, of the order of 10^{-4} eV per tesla.
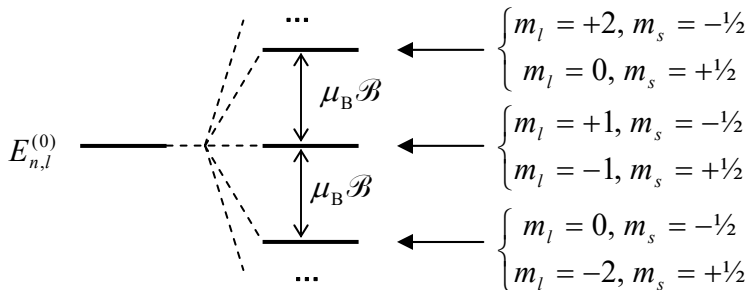

Fig. 6.5. The Paschen-Back effect.

[17] Despite its smallness, the quadratic term is necessary for a description of the negative contribution of the orbital motion to the magnetic susceptibility χ_m (the so-called *orbital diamagnetism*, see EM Sec. 5.5), whose analysis, using Eq. (63), is left for the reader's exercise.
[18] See, e.g., EM Sec. 5.4, in particular, Eqs. (5.95) and (5.100).

Note that all these levels, besides the top and bottom ones, remain doubly degenerate. This limit of the Zeeman effect is sometimes called the *Paschen-Back effect* – whose simplicity was recognized only in the 1920s, due to the need in very high magnetic fields for its observation.

In the opposite limit of relatively *low* magnetic fields, the Zeeman effect takes place on the background of the much larger fine-structure splitting. As was discussed in Sec. 3, at $\mathscr{B} = 0$ each split sub-level has a $2\times(2j + 1)$-fold degeneracy corresponding to $(2j + 1)$ different values of the half-integer quantum number m_j, ranging from $-j$ to $+j$, and two values of the integer $l = j \mp \frac{1}{2}$ – see Fig. 4.[19] The magnetic field lifts this degeneracy. Indeed, in the coupled representation discussed in Sec. 5.7, the perturbation (65) is described by the matrix with elements

$$
H^{(1)} = \frac{e\mathscr{B}}{2m_e}\left\langle j,m_j \left| \hat{L}_z + 2\hat{S}_z \right| j',m_{j'} \right\rangle \equiv \frac{e\mathscr{B}}{2m_e}\left\langle j,m_j \left| \hat{J}_z + \hat{S}_z \right| j',m_{j'} \right\rangle
$$
$$
= \frac{e\mathscr{B}}{2m_e}\left(\hbar m_j \delta_{m_j m_{j'}} + \left\langle j,m_j \left| \hat{S}_z \right| j',m_{j'} \right\rangle \right). \tag{6.67}
$$

To spell out the second term, let us use the general expansion (5.183) for the particular case $s = \frac{1}{2}$, when (as was discussed at the end of Sec. 5.7) it has at most two non-vanishing terms, with the Clebsh-Gordan coefficients (5.190):

$$
\left| j = l \pm \tfrac{1}{2}, m_j \right\rangle
$$
$$
= \pm\left(\frac{l \pm m_j + \frac{1}{2}}{2l+1} \right)^{1/2} \left| m_l = m_j - \tfrac{1}{2}, m_s = +\tfrac{1}{2} \right\rangle + \left(\frac{l \mp m_j + \frac{1}{2}}{2l+1} \right)^{1/2} \left| m_l = m_j + \tfrac{1}{2}, m_s = -\tfrac{1}{2} \right\rangle. \tag{6.68}
$$

Taking into account that the operator $\hat{S}_z$ gives non-zero brackets only for $m_s = m_{s'}$, the 2×2 matrix of elements $\left\langle m_l = m_j \pm \tfrac{1}{2}, m_s = \mp\tfrac{1}{2} \left| \hat{S}_z \right| m_l = m_j \pm \tfrac{1}{2}, m_s = \mp\tfrac{1}{2} \right\rangle$ is diagonal, so we may use Eq. (27) to get

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$$
E - E^{(0)} = \frac{e\mathscr{B}}{2m_e}\left[\hbar m_j + \frac{\hbar}{2}\frac{\left(l \pm m_j + \frac{1}{2}\right)}{2l+1} - \frac{\hbar}{2}\frac{\left(l \mp m_j + \frac{1}{2}\right)}{2l+1} \right]
$$
$$
\equiv \frac{e\mathscr{B}}{2m_e}\hbar m_j\left(1 \pm \frac{1}{2l+1}\right) \equiv \mu_B \mathscr{B} m_j\left(1 \pm \frac{1}{2l+1}\right), \quad \text{for} -j \le m_j \le +j, \tag{6.69}
$$

</div>

where the two signs correspond to the two possible values of $l = j \mp \frac{1}{2}$ – see Fig. 6.
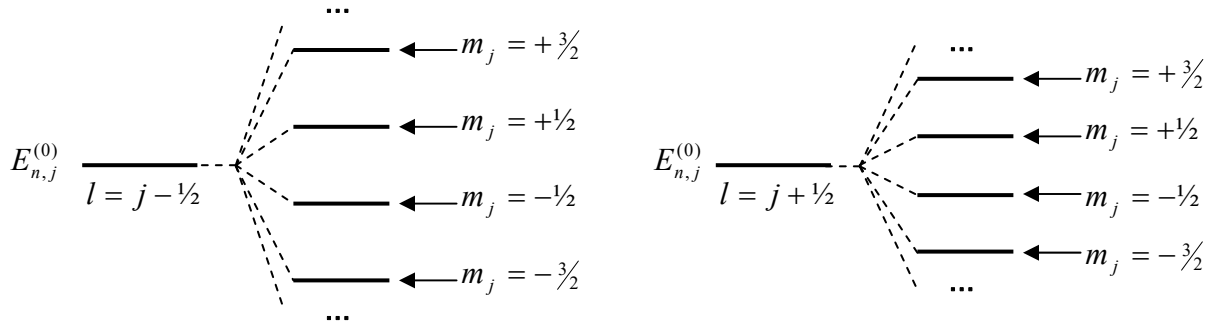

Fig. 6.6. The anomalous Zeeman effect in a hydrogen-like atom/ion.

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[19] In the almost-hydrogen-like, but more complex atoms (such as those of alkali metals), the degeneracy in l may be lifted by electron-electron Coulomb interaction even in the absence of an external magnetic field.

We see that the magnetic field splits each sub-level of the fine structure, with a given l, into $2j + 1$ equidistant levels, with the distance between the levels depending on l. In the late 1890s when this effect was first observed (by T. Preston), there was no notion of spin at all, so this puzzling result was called the *anomalous Zeeman effect*.[20]

The strict quantum-mechanical analysis of the anomalous Zeeman effect for arbitrary s (which is important for applications to multi-electron atoms) is conceptually not too complex but requires explicit expressions for the corresponding Clebsch-Gordan coefficients, which are rather bulky. Let me just cite the unexpectedly simple result of this analysis:

$$\Delta E = \mu_{\mathrm{B}} \mathcal{B} m_j g,$$ (6.70a)

where g is the so-called *Lande factor*:[21]

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$ (6.70b)

Anomalous Zeeman effect for arbitrary s

For $s = \frac{1}{2}$ (and hence $j = l \pm \frac{1}{2}$), this factor is reduced to the parentheses in the last forms of Eq. (69).

It is remarkable that Eqs. (70) may be readily derived using very plausible classical arguments, similar to those used in Sec. 5.7 – see Fig. 5.13 and its discussion. As was discussed in Sec. 5.6, in the absence of spin, the quantization of the observable L_z is a modification of the classical picture of the torque-induced precession of the vector $\mathbf{L}$ about the magnetic field's direction, so the interaction energy, proportional to $\mathcal{B}L_z = \boldsymbol{\mathcal{B}} \cdot \mathbf{L}$, remains constant – see Fig. 7a. On the other hand, at the spin-orbit interaction without an external magnetic field, the Hamiltonian function of the system includes the product $\mathbf{S} \cdot \mathbf{L}$, so in the stationary state it has to be constant, together with J^2, L^2, and S^2. Hence, this system's classical image is a joint precession of the vectors $\mathbf{S}$ and $\mathbf{L}$ about the direction of the vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$, in such a manner that the spin-orbit interaction energy, proportional to the product $\mathbf{L} \cdot \mathbf{S}$, remains constant (Fig. 7b). On this backdrop, the anomalous Zeeman effect in a relatively weak magnetic field $\boldsymbol{\mathcal{B}} = \mathcal{B}\mathbf{n}_z$ corresponds to a much slower additional precession of the vector $\mathbf{J}$ about the z-axis, "dragging" with it the vectors $\mathbf{L}$ and $\mathbf{S}$, rapidly rotating around it.
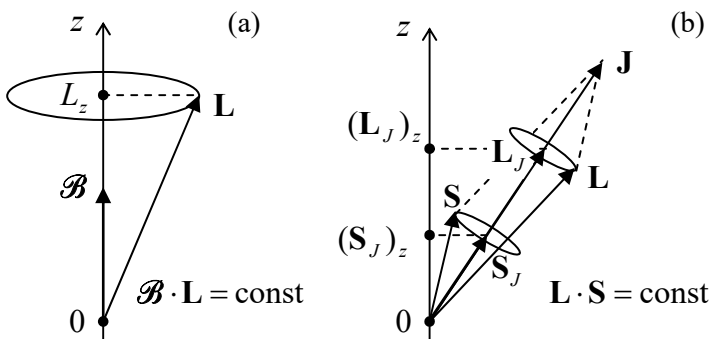

Fig. 6.7. Classical images of (a) the orbital angular momentum's quantization in a magnetic field, and (b) the fine-structure level splitting.

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[20] In this terminology, the *normal Zeeman effect*, observed in atoms with zero net spin, is the one with no spin splitting, i.e. without the second terms in the parentheses of Eqs. (66), (67), and (69).
[21] This formula is frequently used with capital letters J, S, and L, which denote the quantum numbers of the atom as a whole.

This physical picture allows us to conjecture that what is important for the slow precession rate are only the vectors $\mathbf{L}$ and $\mathbf{S}$ averaged over the period of their much faster precession around vector $\mathbf{J}$ – in other words, only their components $\mathbf{L}_J$ and $\mathbf{S}_J$ along the vector $\mathbf{J}$. Classically, these components may be calculated as

$$\mathbf{L}_J = \frac{\mathbf{L} \cdot \mathbf{J}}{J^2} \mathbf{J}, \qquad \text{and } \mathbf{S}_J = \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} \mathbf{J}. \tag{6.71}$$

The scalar products participating in these expressions may be readily expressed via the squared lengths of the vectors, using the following geometric formulas:

$$S^2 = (\mathbf{J} - \mathbf{L})^2 \equiv J^2 + L^2 - 2\mathbf{L} \cdot \mathbf{J}, \qquad L^2 = (\mathbf{J} - \mathbf{S})^2 \equiv J^2 + S^2 - 2\mathbf{J} \cdot \mathbf{S}. \tag{6.72}$$

As a result, we get the following time average:

$$
\begin{aligned}
\overline{L_z + 2S_z} &= \left(\mathbf{L}_J + 2\mathbf{S}_J\right)_z = \left(\frac{\mathbf{L} \cdot \mathbf{J}}{J^2}\mathbf{J} + 2\frac{\mathbf{S} \cdot \mathbf{J}}{J^2}\mathbf{J}\right)_z = \frac{J_z}{J^2}\left(\mathbf{L} \cdot \mathbf{J} + 2\mathbf{S} \cdot \mathbf{J}\right) \\
&= J_z \frac{(J^2 + L^2 - S^2) + 2(J^2 + S^2 - L^2)}{2J^2} \equiv J_z\left(1 + \frac{J^2 + S^2 - L^2}{2J^2}\right).
\end{aligned}
\tag{6.73}
$$

The last move is to smuggle in some quantum mechanics by using, instead of the vector lengths squared and the z-component of J_z, their eigenvalues given by Eqs. (5.169), (5.175), and (5.177). As a result, we immediately arrive at the exact Eqs. (70). This coincidence encourages thinking about quantum mechanics of angular momenta in the classical terms of torque-induced precession, which turns out to be very fruitful in some more complex problems of atomic and molecular physics.

The high-field limit and low-field limits of the Zeeman effect, described respectively by Eqs. (66) and (69), are separated by a medium field range, in which the Zeeman splitting is of the order of the fine-structure splitting analyzed in Sec. 3. There is no time in this course for a quantitative analysis of this (conceptually simple) crossover, which involves rather cumbersome algebra.[22]

6.5. Time-dependent perturbations

Now let us proceed to the case when the perturbation $\hat{H}^{(1)}$ in Eq. (1) is a function of time, while $\hat{H}^{(0)}$ is time-independent. The adequate perturbative approach to this problem, and its results, depend critically on the relation between the characteristic frequency ω of the perturbation and the distance between the initial system's energy levels:

$$\hbar\omega \leftrightarrow |E_n - E_{n'}|. \tag{6.74}$$

In the case when all essential frequencies of a perturbation are very small in the sense of Eq. (74), we are dealing with the so-called *adiabatic* change of parameters, that may be treated essentially as a time-independent perturbation – see the previous sections of this chapter). The most interesting observation here is that the adiabatic perturbation does not allow any significant transfer of the system's

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[22] For a more complete discussion of the Stark, Zeeman, and fine-structure effects in atoms, I can recommend, for example, either the monograph by G. Woolgate cited above, or the one by I. Sobelman, *Theory of Atomic Spectra*, Alpha Science, 2006.

probability from one eigenstate to another. For example, in the WKB limit of the orbital motion, the Bohr quantization rule and its Wilson-Sommerfeld modification (2.110) guarantee that the integral

$$\oint_C \mathbf{p} \cdot d\mathbf{r} \,, \tag{6.75}$$

taken along the particle's classical trajectory, is an *adiabatic invariant*, i.e. does not change at a slow change of system's parameters. (It is curious that classical mechanics also guarantees the invariance of the integral (75), but its proof there[23] is much harder than the quantum-mechanical derivation of this fact, carried out in Sec. 2.4.) This is why even if the perturbation becomes large with time (while changing sufficiently slowly), we can expect the classification of eigenstates and eigenvalues to persist.

Let us proceed to the harder case when both sides of Eq. (74) are comparable, using for this discussion the Schrödinger picture of quantum dynamics, given by Eq. (4.158). Combining it with Eq. (1), we get the Schrödinger equation in the form

$$i\hbar \frac{\partial}{\partial t} |\alpha(t)\rangle = \left(\hat{H}^{(0)} + H^{(1)}(t)\right) |\alpha(t)\rangle. \tag{6.76}$$

Very much in the spirit of our treatment of the time-independent case in Sec. 1, let us represent the time-dependent ket-vector of the system with its expansion,

$$|\alpha(t)\rangle = \sum_n |n\rangle \langle n|\alpha(t)\rangle, \tag{6.77}$$

over the full and orthonormal set of the unperturbed, stationary ket-vectors defined by the equation

$$\hat{H}^{(0)} |n\rangle = E_n |n\rangle. \tag{6.78}$$

(Note that these kets $|n\rangle$ are exactly what was called $|n^{(0)}\rangle$ in Sec. 1; we may afford a less bulky notation in this section because only the lowest orders of the perturbation theory will be discussed.) Plugging the expansion (77), with n replaced with n', into both sides of Eq. (76), and then inner-multiplying both its sides by the bra-vector $\langle n|$ of another unperturbed (and hence time-independent) state of the system, we get the following set of linear, ordinary differential equations for the expansion coefficients:

$$i\hbar \frac{d}{dt} \langle n|\alpha(t)\rangle = E_n \langle n|\alpha(t)\rangle + \sum_{n'} H^{(1)}_{nn'}(t) \langle n'|\alpha(t)\rangle, \tag{6.79}$$

where the matrix elements of the perturbation, in the *unperturbed* state basis, defined similarly to Eq. (8), are now functions of time:

$$H^{(1)}_{nn'}(t) \equiv \langle n|\hat{H}^{(1)}(t)|n'\rangle. \tag{6.80}$$

The set of differential equations (79), which are still exact, may be useful for numerical calculations.[24] However, it has a certain technical inconvenience, which becomes clear if we consider its (evident) solution in the absence of perturbation:[25]

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[23] See, e.g., CM Sec. 10.2.

[24] Even if the problem under analysis may be described by the wave-mechanics Schrödinger equation (1.25), direct numerical integration of that *partial* differential equation is typically less convenient than that of the *ordinary* differential equations (79).

[25] This is of course just a more general form of Eq. (1.62) of the wave mechanics of time-independent systems.

$$\langle n|\alpha(t)\rangle = \langle n|\alpha(0)\rangle \exp\left\{-i\frac{E_n}{\hbar}t\right\}. \tag{6.81}$$

We see that these solutions oscillate very fast, and their numerical modeling may represent a challenge for even the fastest computers. These spurious oscillations (whose frequency, in particular, depends on the energy reference level) may be partly tamed by looking for the general solution of Eqs. (79) in a form inspired by Eq. (81):

$$\langle n|\alpha(t)\rangle \equiv a_n(t) \exp\left\{-i\frac{E_n}{\hbar}t\right\}. \tag{6.82}$$

Here $a_n(t)$ are new functions of time (essentially, the stationary states' probability amplitudes), which may be used, in particular, to calculate the time-dependent *level occupancies*, i.e. the probabilities W_n to find the perturbed system on the corresponding energy levels of the unperturbed system:

$$W_n(t) = |\langle n|\alpha(t)\rangle|^2 = |a_n(t)|^2. \tag{6.83}$$

Plugging Eq. (82) into Eq. (79), for these functions, we readily get a slightly modified system of equations:

$$\boxed{i\hbar\dot{a}_n = \sum_{n'} a_{n'} H^{(1)}_{nn'}(t) e^{i\omega_{nn'}t},} \tag{6.84}$$

where the factors $\omega_{nn'}$, defined by the relation

$$\boxed{\hbar\omega_{nn'} \equiv E_n - E_{n'},} \tag{6.85}$$

have the physical sense of frequencies of *potential* quantum transitions between the nth and n'^{th} energy levels of the unperturbed system. (The conditions when such transitions indeed take place will be clear soon.) The advantages of Eq. (84) over Eq. (79), for both analytical and numerical calculations, are their independence of the energy reference, and lower frequencies of oscillations of the right-hand side terms, especially when the energy levels of interest are close to each other.[26]

In order to continue our analytical treatment, let us focus on a particular but very important problem of a sinusoidal perturbation *turned on* at some moment – which may be taken for $t = 0$:

$$\boxed{\hat{H}^{(1)}(t) = \begin{cases} 0, & \text{for } t < 0, \\ \hat{A}e^{-i\omega t} + \hat{A}^\dagger e^{+i\omega t}, & \text{for } t \geq 0, \end{cases}} \tag{6.86}$$

where the *perturbation amplitude operators* $\hat{A}$ and $\hat{A}^\dagger$,[27] and hence their matrix elements,

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[26] Note that the relation of Eq. (84) to the initial Eq. (79) is very close to the relation of the interaction picture of quantum dynamics, discussed at the end of Sec. 4.6, to its Schrödinger picture, with the perturbation Hamiltonian playing the role of the interaction one – compare Eqs. (1) and Eq. (4.206). Indeed, Eq. (84) could be readily obtained from the interaction picture, and I did not do this just to avoid using this heavy bra-ket artillery for our current (relatively) simple problem, and hence to keep its physics more transparent.

[27] The notation of the amplitude operators in Eq. (86) is justified by the fact that the perturbation Hamiltonian has to be self-adjoint (Hermitian), and hence each term on the right-hand side of that relation has to be a Hermitian conjugate of its counterpart, which is evidently true only if the amplitude operators are also the Hermitian conjugates of each other. Note, however, that each of these amplitude operators is generally *not* Hermitian.

$$\langle n|\hat{A}|n'\rangle \equiv A_{nn'}, \qquad \langle n|\hat{A}^\dagger|n'\rangle = A_{n'n}^*, \tag{6.87}$$

are time-independent after the turn-on moment. In this case, Eq. (84) yields

$$i\hbar\dot{a}_n = \sum_{n'} a_{n'}\left[A_{nn'}e^{i(\omega_{nn'}-\omega)t} + A_{n'n}^*e^{i(\omega_{nn'}+\omega)t}\right], \qquad \text{for } t > 0. \tag{6.88}$$

This is, generally, still a nontrivial system of coupled differential equations; however, it allows simple and explicit solutions in two very important limits. First, let us assume that our system initially was definitely in one eigenstate n' (usually, though not necessarily, in the ground state), and that the occupancies W_n of all other levels stay very low all the time. (We will find the condition when the second assumption is valid *a posteriori* – from the solution.) With these assumptions,

$$a_{n'} = 1; \qquad |a_n| << 1, \quad \text{for } n \ne n', \tag{6.89}$$

Eq. (88) may be readily integrated, giving

$$a_n = -\frac{A_{nn'}}{\hbar(\omega_{nn'}-\omega)}\left[e^{i(\omega_{nn'}-\omega)t}-1\right] - \frac{A_{n'n}^*}{\hbar(\omega_{nn'}+\omega)}\left[e^{i(\omega_{nn'}+\omega)t}-1\right], \qquad \text{for } n \ne n'. \tag{6.90}$$

This expression describes what is colloquially called the *ac excitation of* (other) *energy levels*. Qualitatively, it shows that the probability W_n (83) of finding the system in each state ("on each energy level") of the system does not tend to any constant value but rather oscillates in time. It also shows that the ac-field-induced transfer of the system from one state to the other one has a clearly resonant character: the maximum occupancy W_n of a level with number $n \ne n'$ grows infinitely when the corresponding *detuning*[28]

$$\Delta_{nn'} \equiv \omega - \omega_{nn'}, \tag{6.91}$$

tends to zero. This conclusion is clearly unrealistic, and is an artifact of our initial assumption (89); according to Eq. (90), it is satisfied only if[29]

$$|A_{nn'}| << \hbar|\omega \pm \omega_{nn'}|, \tag{6.92}$$

and hence which does not allow a deeper analysis of the resonant excitation.

In order to overcome this limitation, we may perform the following trick – very similar to the one we used for the transfer to the degenerate case in Sec. 1. Let us assume that for a certain level n,

$$|\Delta_{nn'}| << \omega, |\omega \pm \omega_{n''n}|, |\omega \pm \omega_{n''n'}|, \qquad \text{for all } n'' \ne n, n' \tag{6.93}$$

– the condition illustrated in Fig. 8. Then, according to Eq. (90), we may ignore the occupancy of all but two levels, n and n', and also the second, non-resonant term with frequency $\omega_{nn'} + \omega \approx 2\omega >> |\Delta_{nn'}|$ in Eqs. (88),[30] now written for two probability amplitudes, a_n and $a_{n'}$.

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[28] The notion of detuning is also very useful in the classical theory of oscillations (see, e.g., CM Chapter 5), where the role of $\omega_{nn'}$ is played by the own frequency ω_0 of the oscillator.

[29] Strictly speaking, one more condition is that the number of "resonance" levels is also not too high – see Sec. 6.

[30] The second assumption, i.e. the omission of non-resonant terms in the equations for amplitudes is called the *Rotating Wave Approximation* (RWA); the same idea in the classical theory of oscillations is the basis of what is usually called the *van der Pol method*, and its result, the *reduced equations* – see, e.g., CM Secs. 5.3-5.5.
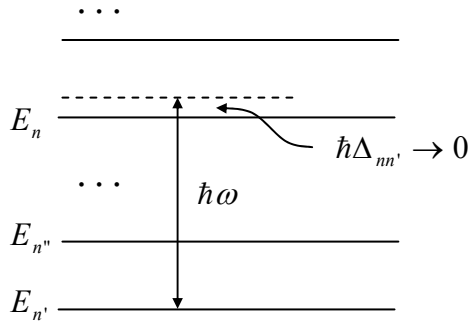
Fig. 6.8. The resonant excitation of an energy level.

The result is the following system of two linear equations:

$$i\hbar\dot{a}_n = a_{n'}A e^{-i\Delta t}, \qquad i\hbar\dot{a}_{n'} = a_n A^* e^{i\Delta t}, \qquad (6.94)$$

which uses the shorthand notation $A \equiv A_{nn'}$ and $\Delta \equiv \Delta_{nn'}$. (I will use this simplified notation for a while – until other energy levels become involved, at the beginning of the next section). This system may be readily reduced to a form without explicit time dependence of the right-hand parts – for example, by introducing the following new probability amplitudes, with the same moduli:

$$b_n \equiv a_n e^{i\Delta t/2}, \qquad b_{n'} \equiv a_{n'} e^{-i\Delta t/2}, \qquad (6.95)$$

so

$$a_n = b_n e^{-i\Delta t/2}, \quad a_{n'} = b_{n'} e^{i\Delta t/2}. \qquad (6.96)$$

Plugging these relations into Eq. (94), we get two usual linear first-order differential equations:

$$i\hbar\dot{b}_n = -\frac{\hbar\Delta}{2}b_n + A b_{n'}, \qquad i\hbar\dot{b}_{n'} = A^* b_n + \frac{\hbar\Delta}{2}b_{n'}. \qquad (6.97)$$

As the reader knows very well by now, the general solution of such a system is a linear combination of two exponential functions, $\exp\{\lambda_\pm t\}$, with the exponents $\lambda_\pm$ that may be found by plugging any of these functions into Eq. (97), and requiring the consistency of the two resulting linear algebraic equations. In our case, the consistency condition (i.e. the characteristic equation of the system) is

$$\begin{vmatrix} -\hbar\Delta/2 - i\hbar\lambda_\pm & A \\ A^* & \hbar\Delta/2 - i\hbar\lambda_\pm \end{vmatrix} = 0, \qquad (6.98)$$

and has two solutions $\lambda_\pm = \pm i\Omega$, where

$$\boxed{\Omega \equiv \left(\frac{\Delta^2}{4} + \frac{|A|^2}{\hbar^2}\right)^{1/2}, \qquad \text{i.e. } 2\Omega = \left(\Delta^2 + 4\frac{|A|^2}{\hbar^2}\right)^{1/2}.} \qquad (6.99)$$

The coefficients at the exponents are determined by initial conditions. If, as was assumed before, the system was on the level n' initially (at $t = 0$), i.e. if $a_{n'}(0) = 1$, $a_n(0) = 0$, so $b_{n'}(0) = 1$, $b_n(0) = 0$ as well, then Eqs. (97) yield, in particular:

$$b_n(t) = -i\frac{A}{\hbar\Omega}\sin\Omega t, \qquad (6.100)$$

so the nth level occupancy is

$$W_n = |b_n|^2 = \frac{|A|^2}{\hbar^2 \Omega^2} \sin^2 \Omega t \equiv \frac{|A|^2}{|A|^2 + (\hbar\Delta/2)^2} \sin^2 \Omega t .$$

(6.101)   Rabi formula

This is the famous *Rabi oscillation formula*.[31] It shows that if the detuning is large in comparison with $|A|/\hbar$, though still small in the sense of Eq. (93), the frequency 2Ω of the Rabi oscillations is completely determined by the detuning, and their amplitude is small:

$$W_n(t) = 4\frac{|A|^2}{\hbar^2 \Delta^2} \sin^2 \frac{\Delta t}{2} \ll 1, \qquad \text{for } |A|^2 \ll (\hbar\Delta)^2 ,$$

(6.102)

– the result which could be obtained directly from Eq. (90), just neglecting the second term on its right-hand side. However, now we may also analyze the results of an increase of the perturbation amplitude: it leads not only to an increase of the amplitude of the probability oscillations but also of their frequency – see Fig. 9. Ultimately, at $|A| \gg \hbar|\Delta|$ (for example, at the exact resonance, $\Delta = 0.$, i.e. $\omega_{nn'} = \omega$, so $E_n = E_{n'} + \hbar\omega$), Eqs. (101)-(102) give $\Omega = |A|/\hbar$ and $(W_n)_{max} = 1$, i.e. describe a periodic, full "repumping" of the system from one level to another and back, with a frequency proportional to the perturbation amplitude.[32]
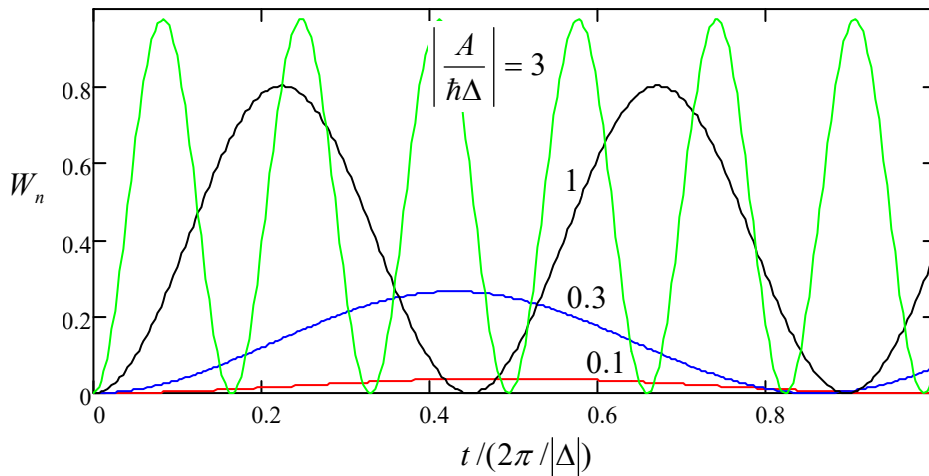

Fig. 6.9. The Rabi oscillations for several values of the normalized amplitude of ac perturbation.

This effect is a close analog of the quantum oscillations in two-level systems with time-independent Hamiltonians, which were discussed in Secs. 2.6 and 5.1. Indeed, let us revisit, for a moment, their discussion started at the end of Sec.1 of this chapter, now paying more attention to the time evolution of the system under a perturbation. As was argued in that section, the most general perturbation Hamiltonian lifting the two-fold degeneracy of an energy level, in an arbitrary basis, has the matrix (28). Let us describe the system's dynamics using, again, the Schrödinger picture, representing the ket-vector of an arbitrary state of the system in the form (5.1), where $\uparrow$ and $\downarrow$ are the

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[31] It was derived in 1952 by Isaac Rabi, in the context of his group's pioneering experiments with the ac (practically, microwave) excitation of quantum states, using molecular beams in vacuum.

[32] As Eqs. (82), (96), and (99) show, the lowest frequency in the system is $\omega_1 = \omega_{n'} - \Delta/2 + \Omega$, so at $A \to 0$, $\hbar\omega_1 \approx \hbar\omega_{n'} + 2|A|^2/\hbar\Delta$. This effective shift of the lowest energy level (which may be measured by another "probe" field of a different frequency) is a particular case of the *ac Stark effect*, which was already mentioned in Sec. 2.

time-independent states of the basis in that Eq. (28) is written (now without any obligation to associate these states with the z-basis of any spin-½.) Then, the Schrödinger equation (4.158) yields

$$i\hbar\begin{pmatrix} \dot{\alpha}_\uparrow \\ \dot{\alpha}_\downarrow \end{pmatrix} = \mathrm{H}^{(1)}\begin{pmatrix} \alpha_\uparrow \\ \alpha_\downarrow \end{pmatrix} \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} \alpha_\uparrow \\ \alpha_\downarrow \end{pmatrix} \equiv \begin{pmatrix} H_{11}\alpha_\uparrow + H_{12}\alpha_\downarrow \\ H_{21}\alpha_\uparrow + H_{22}\alpha_\downarrow \end{pmatrix}. \tag{6.103}$$

As we know (for example, from the discussion in Sec. 5.1), the average of the diagonal elements of the matrix gives just a common shift of the system's energy; for the purpose of the analysis, it may be absorbed into the energy reference level. Also, the Hamiltonian operator has to be Hermitian, so the off-diagonal elements of its matrix have to be complex-conjugate. With this, Eqs. (103) are reduced to the form,

$$i\hbar\dot{\alpha}_\uparrow = -\frac{\xi}{2}\alpha_\uparrow + H_{12}\alpha_\downarrow, \qquad i\hbar\dot{\alpha}_\downarrow = H_{12}^*\alpha_\uparrow + \frac{\xi}{2}\alpha_\downarrow, \qquad \text{with } \hbar\xi \equiv H_{22} - H_{11}, \tag{6.104}$$

which is absolutely similar to Eqs. (97). In particular, these equations describe the quantum oscillations of the probabilities $W_\uparrow = |\alpha_\uparrow|^2$ and $W_\downarrow = |\alpha_\downarrow|^2$ with the frequency[33]

$$2\Omega = \left(\xi^2 + 4\frac{|H_{12}|^2}{\hbar^2} \right)^{1/2}. \tag{6.105}$$

The similarity of Eqs. (97) and (104), and hence of Eqs. (99) and (105), shows that the "usual" quantum oscillations and the Rabi oscillations have essentially the same physical nature, besides that in the latter case the external ac signal quantum $\hbar\omega$ bridges the separated energy levels, effectively reducing their difference $(E_n - E_{n'})$ to a much smaller difference $-\Delta \equiv (E_n - E_{n'}) - \hbar\omega$. Also, since the Hamiltonian (28) is similar to that given by Eq. (5.2), the dynamics of such a system with two ac-coupled energy levels, within the limits (93) of the perturbation theory, is completely similar to that of a time-independent two-level system. In particular, its state may be similarly represented by a point on the Bloch sphere shown in Fig. 5.3, with its dynamics described, in the Heisenberg picture, by Eq. (5.19). This fact is very convenient for the experimental implementation of quantum information processing systems (to be discussed in more detail in Sec. 8.5), because it enables qubit manipulations in a broad variety of physical systems with well-separated energy levels, using external ac (usually either microwave or optical) sources.

Note, however, that according to Eq. (90), if a system has energy levels other than n and n', they also become occupied to some extent. Since the sum of all occupancies equals 1, this means that $(W_n)_{\max}$ may approach 1 only if the other excitation amplitude is very small, and hence the state manipulation time scale $\mathcal{T} = 2\pi/\Omega = 2\pi\hbar/|A|$ is very long. The ultimate limit in this sense is provided by the harmonic oscillator where all energy levels are equidistant, and the probability repumping between all of them occurs at comparable rates. In particular, in this system, the implementation of the full Rabi oscillations is impossible even at the exact resonance.[34]

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[33] By the way, Eq. (105) gives a natural generalization of the relations obtained for the frequency of such oscillations in Sec. 2.6, where the coupled potential wells were assumed to be exactly similar, so $\xi = 0$. Moreover, Eqs. (104) gives a long-promised proof of Eqs. (2.201), and hence a better justification of Eqs. (2.203).

[34] From Sec. 5.5, we already know what happens to the ground state of an oscillator at its external sinusoidal (or any other) excitation: it turns into a Glauber state, i.e. a superposition of *all* Fock states – see Eq. (5.134).

However, I would not like these quantitative details to obscure from the reader the most important qualitative (OK, maybe semi-quantitative :-) conclusion of this section's analysis: a resonant increase of the interlevel transition intensity at $\omega \to \omega_{nn'}$. As will be shown later in the course, in a quantum system coupled to its environment at least slightly (hence in reality, in *any* quantum system), such increase is accompanied by a sharp increase of the external field's *absorption*, which may be measured. This increase is used in numerous applications, notably including the magnetic resonance techniques already mentioned in Sec. 5.1.

6.6. Quantum-mechanical Golden Rule

One of the results of the past section, Eq. (102), may be used to derive one of the most important and nontrivial results of quantum mechanics. For that, let us consider the case when the perturbation causes quantum transitions from a *discrete* energy level $E_{n'}$ into a group of eigenstates with a very dense (essentially *continuous*) spectrum E_n – see Fig. 10a.
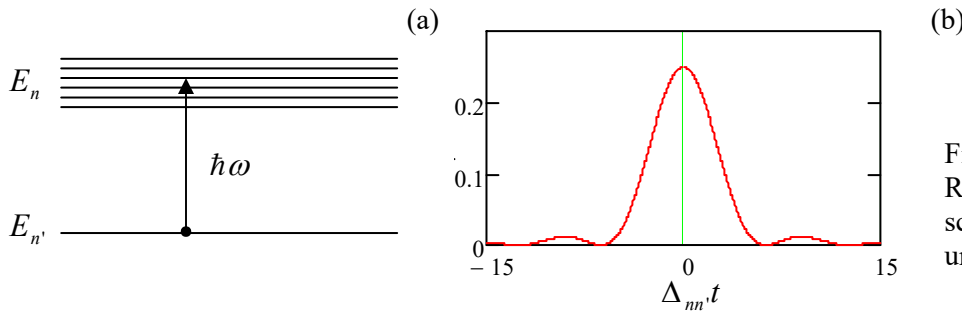

Fig. 6.10. Deriving the Golden Rule: (a) the energy level scheme, and (b) the function under the integral in Eq. (108).

If, for all states n of the group, the following conditions are satisfied

$$\left|A_{nn'}\right|^2 << \left(\hbar\Delta_{nn'}\right)^2 << \left(\hbar\omega_{nn'}\right)^2, \qquad (6.106)$$

then Eq. (102) coincides with the result that would follow from Eq. (90). This means that we may apply Eq. (102), with the indices n and n' duly restored, to any level n of our tight group. As a result, the total probability of having our system transferred from the initial level n' to that group is

$$W_\Sigma(t) = \sum_n W_n(t) = \frac{4}{\hbar^2}\sum_n \frac{\left|A_{nn'}\right|^2}{\Delta_{nn'}^2}\sin^2\frac{\Delta_{nn'}t}{2}. \qquad (6.107)$$

Now comes the main, absolutely beautiful trick: let us assume that the summation over n is limited to a tight group of very similar states whose matrix elements $A_{nn'}$ are virtually similar (we will check the validity of this assumption later on), so we can take $|A_{nn'}|^2$ out of the sum in Eq. (107) and then replace the sum with the corresponding integral:

$$W_\Sigma(t) = \frac{4|A_{nn'}|^2}{\hbar^2}\int\frac{1}{\Delta_{nn'}^2}\sin^2\frac{\Delta_{nn'}t}{2}dn \equiv \frac{4|A_{nn'}|^2\rho_n t}{\hbar}\int\frac{1}{\left(\Delta_{nn'}t\right)^2}\sin^2\frac{\Delta_{nn'}t}{2}d(-\Delta_{nn'}t), \qquad (6.108)$$

where ρ_n is the density of the states n on the energy axis:

$$\boxed{\rho_n \equiv \frac{dn}{dE_n}.} \qquad (6.109)$$

Density of states

This density and the matrix element $A_{nn'}$ have to be evaluated at $\Delta_{nn'} = 0$, i.e. at energy $E_n = E_{n'} + \hbar\omega$, and are assumed to be constant within the final state group. At fixed $E_{n'}$, the function under integral (108) is even and decreases fast at $|\Delta_{nn'}t| \gg 1$ – see Fig. 10b. Hence we may introduce a dimensionless integration variable $\xi \equiv \Delta_{nn'}t$, and extend the integration over it formally from $-\infty$ to $+\infty$. Then the integral in Eq. (108) is reduced to a table one,[35] and yields

$$W_\Sigma(t) = \frac{4|A_{nn'}|^2 \rho_n t}{\hbar} \int_{-\infty}^{+\infty} \frac{1}{\xi^2} \sin^2 \frac{\xi}{2} d\xi = \frac{4|A_{nn'}|^2 \rho_n t}{\hbar} \frac{\pi}{2} \equiv \Gamma t , \qquad (6.110)$$

where the constant

$$\boxed{\Gamma = \frac{2\pi}{\hbar} |A_{nn'}|^2 \rho_n} \qquad (6.111)$$

is called the *transition rate*.[36] This is one of the most famous and useful results of quantum mechanics, its *Golden Rule*[37], which deserves much discussion.

First of all, let us reproduce the reasoning already used in Sec. 2.5 to show that the meaning of the rate Γ is much deeper than Eq. (110) seems to imply. Indeed, due to the conservation of the total probability, $W_{n'} + W_\Sigma = 1$, we can rewrite that equation as

$$\dot{W}_{n'}\big|_{t=0} = -\Gamma. \qquad (6.112)$$

Evidently, this result cannot be true for all times, otherwise the probability $W_{n'}$ would become negative. The reason for this apparent contradiction is that Eq. (110) was obtained in the assumption that initially, the system was completely on level n': $W_{n'}(0) = 1$. Now, if at the initial moment the value of $W_{n'}$ is different, the result (110) has to be multiplied by that number, due to the linear relation (88) between da_n/dt and $a_{n'}$. Hence, instead of Eq. (112), we get a differential equation similar to Eq. (2.159),

$$\dot{W}_{n'}\big|_{t\geq 0} = -\Gamma W_{n'} , \qquad (6.113)$$

which, for a time-independent Γ, has the evident solution,

$$\boxed{W_{n'}(t) = W_{n'}(0)e^{-\Gamma t} ,} \qquad (6.114)$$

describing the exponential decay of the initial state's occupancy, with the time constant $\tau = 1/\Gamma$.

I am inviting the reader to review this fascinating result again: by the summation of *periodic oscillations* (102) over many levels n, we have got an *exponential decay* (114) of the probability. This trick becomes possible because the effective range ΔE_n of the state energies E_n giving substantial

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[35] See, e.g., MA Eq. (6.12).

[36] In some texts, the density of states in Eq. (111) is replaced with a formal expression $\Sigma_n \delta(E_n - E_{n'} - \hbar\omega)$. Indeed, applied to a finite energy interval ΔE_n with $\Delta n \gg 1$ levels, it gives the same result: $\Delta n \equiv (dn/dE_n)\Delta E_n \equiv \rho_n \Delta E_n$. Such replacement may be technically useful in some cases, but is incorrect for $\Delta n \sim 1$, and hence should be used with the utmost care, so for most applications, the more explicit form (111) is preferable.

[37] Sometimes Eq. (111) is called "Fermi's Golden Rule". This is rather unfair, because this result had been developed mostly by the same P. A. M. Dirac in 1927, and Enrico Fermi's role was not much more than advertising it, under the name of "Golden Rule No. 2", in his influential lecture notes on nuclear physics that were published much later, in 1950. (To be fair to Fermi, he has never tried to pose as the Golden Rule's author.)

contributions to the integral (108), shrinks with time: $\Delta E_n \sim \hbar/t$.[38] However, since most of the decay (114) takes place within the time interval of the order of $\tau \equiv 1/\Gamma$, the range of the participating final energies may be estimated as

$$\Delta E_n \sim \frac{\hbar}{\tau} \equiv \hbar\Gamma . \qquad (6.115)$$

This estimate is very instrumental for the formulation of conditions of the Golden Rule's validity. First, we have assumed that the matrix elements of the perturbation and the density of states are independent of the energy within the interval (115). This gives the following requirement

$$\Delta E_n \sim \hbar\Gamma << E_n - E_{n'} \sim \hbar\omega , \qquad (6.116)$$

Second, for the transfer from the sum (107) to the integral (108), we need the number of states within that energy interval, $\Delta N_n = \rho_n \Delta E_n$, to be much larger than 1. Merging Eq. (116) with Eq. (92) for all the energy levels $n'' \neq n, n'$ not participating in the resonant transition, we may summarize all conditions of the Golden Rule validity as

$$\rho_n^{-1} << \hbar\Gamma << \hbar\left|\omega \pm \omega_{n'n''}\right|. \qquad (6.117)$$

(The reader may ask whether I have neglected the condition expressed by the first of Eqs. (106). However, for $\Delta_{nn'} \sim \Delta E_n/\hbar \sim \Gamma$, this condition is just $|A_{nn'}|^2 << (\hbar\Gamma)^2$, so plugging it into Eq. (111),

$$\Gamma << \frac{2\pi}{\hbar}(\hbar\Gamma)^2 \rho_n , \qquad (6.118)$$

and canceling one Γ and one $\hbar$, we see that it coincides with the first relation in Eq. (117) above.)

Let us have a look at whether these conditions may be satisfied in practice, at least in some cases. For example, let us consider the optical ionization of an atom, with the released electron confined in a volume of the order of 1 cm$^3 \equiv 10^{-6}$ m^3. According to Eq. (1.90), with E of the order of the atomic ionization energy $E_n - E_{n'} = \hbar\omega \sim 1$ eV, the density of electron states in that volume is of the order of 10^{21} 1/eV, while the right-hand side of Eq. (117) is of the order of $E_n \sim 1$ eV. Thus the conditions (117) provide an approximately 20-orders-of-magnitude range for acceptable values of $\hbar\Gamma$. This illustration should give the reader a taste of why the Golden Rule is applicable to so many situations.

The physical picture of the initial state's decay is also very important. According to Eq. (114), the external excitation transfers the system into the continuous spectrum of levels n, and it never comes back to the initial level n'. However, it was derived from the quantum mechanics of Hamiltonian systems, whose equations are invariant with respect to time reversal.[39] This paradox is a result of our generalization (113) of the exact result (112) This trick, breaking the time-reversal symmetry, is absolutely adequate for the physics under study. Indeed, some gut feeling of the physical sense of the resulting irreversibility may be obtained from the following observation. As Eq. (1.86) illustrates, the distance between the adjacent orbital energy levels tends to zero only if the system's size goes to infinity. This means that our assumption of the continuous energy spectrum of the finial states n

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[38] This is one more appearance of the "energy-time uncertainty relation", which was discussed in Sec. 2.5.

[39] This situation is similar to the irreversible increase of entropy of macroscopic systems, despite the fact that their microscopic components obey reversible laws of motion, which is postulated in thermodynamics and explained in statistical physics – see, e.g., SM Secs. 1.2 and 2.2.

essentially requires these states to be broadly extended in space – being either fully free or virtually free de Broglie waves. Thus the Golden Rule corresponds to the (physically justified) assumption that in an infinitely large system, the traveling de Broglie waves excited by a local source and propagating outward from it, would never come back, and even if they did, unpredictable phase shifts introduced by minor uncontrollable perturbations on their way would never allow them to sum up in the coherent way necessary to bring the system back into the initial state n'. (This is essentially the same situation that was discussed, for a particular 1D wave-mechanical system, in Sec. 2.5.)

To get a feeling of the Golden Rule at work, let us apply it to the following simple problem – which is a toy model of the photoelectric effect, briefly discussed in Sec. 1.1(ii). A 1D particle is initially trapped in the ground state of a narrow potential well described by Eq. (2.158):

$$U(x) = -\mathcal{W}\delta(x), \qquad \text{with } \mathcal{W} > 0. \tag{6.119}$$

Let us calculate the rate Γ of the particle's "ionization" (i.e. its excitation into a group of extended, delocalized states) by a weak classical sinusoidal force of amplitude F_0 and frequency ω, suddenly turned on at some instant, say $t = 0$.

As a reminder, the initial localized state (in our current notation, n') of such a particle was already found in Sec. 2.6:

$$\psi_{n'}(x) = \kappa^{1/2} \exp\{-\kappa|x|\}, \qquad \text{with } \kappa \equiv \frac{m\mathcal{W}}{\hbar^2}, \quad E_{n'} \equiv -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\mathcal{W}^2}{2\hbar^2}. \tag{6.120}$$

The final, extended states n, with a continuous spectrum, for this problem exist only at energies $E_n > 0$, so the excitation rate is different from zero only for frequencies

$$\omega > \omega_{\min} \equiv \frac{|E_{n'}|}{\hbar} = \frac{m\mathcal{W}^2}{2\hbar^3}. \tag{6.121}$$

The weak sinusoidal force may be described by the following perturbation Hamiltonian,

$$\hat{H}^{(1)} = -F(t)\hat{x} = -F_0\hat{x}\cos\omega t \equiv -\frac{F_0}{2}\hat{x}\left(e^{i\omega t} + e^{-i\omega t}\right), \qquad \text{for } t > 0, \tag{6.122}$$

so according to Eq. (86), which serves as the amplitude operator's definition, in this case

$$\hat{A} = \hat{A}^\dagger = -\frac{F_0}{2}\hat{x}. \tag{6.123}$$

The matrix elements $A_{nn'}$ that participate in Eq. (111) may be readily calculated in the coordinate representation:

$$A_{nn'} = \int_{-\infty}^{+\infty}\psi_n^*(x)\hat{A}(x)\psi_{n'}(x)dx = -\frac{F_0}{2}\int_{-\infty}^{+\infty}\psi_n^*(x)x\psi_{n'}(x)dx. \tag{6.124}$$

Since, according to Eq. (120), the initial $\psi_{n'}$ is a *symmetric* function of x, any non-vanishing contributions to this integral are given only by *antisymmetric* functions $\psi_n(x)$, proportional to $\sin k_n x$, with the wave number k_n related to the final energy by the well-familiar equality (1.89):

$$\frac{\hbar^2 k_n^2}{2m} = E_n. \tag{6.125}$$

As we know from Sec. 2.6 (see in particular Eq. (2.167) and its discussion), such antisymmetric functions, with $\psi_n(0) = 0$, are not affected by the zero-centered delta-functional potential (119), so their density ρ_n is the same as that in completely free space, and we could use Eq. (1.93). However, since that relation was derived for traveling waves, it is more prudent to repeat its derivation for standing waves, confining them to an artificial segment $[-l/2, +l/2]$ – long in the sense

$$k_n l, \kappa l \gg 1, \tag{6.126}$$

so it does not affect the initial localized state and the excitation process. Then the confinement requirement $\psi_n(\pm l/2) = 0$ immediately yields the condition $k_n l/2 = n\pi$, so Eq. (1.93) is indeed valid, but only for positive values of k_n, because $\sin k_n x$ with $k_n \to -k_n$ does not describe an independent standing-wave eigenstate. Hence the final state density is

$$\rho_n \equiv \frac{dn}{dE_n} \equiv \frac{dn}{dk_n} \bigg/ \frac{dE_n}{dk_n} = \frac{l}{2\pi} \bigg/ \frac{\hbar^2 k_n}{m} \equiv \frac{lm}{2\pi\hbar^2 k_n}. \tag{6.127}$$

It may look troubling that the density of states depends on the artificial segment's length l, but the same l also participates in the final wavefunctions' normalization factor,[40]

$$\psi_n = \left(\frac{2}{l}\right)^{1/2} \sin k_n x, \tag{6.128}$$

and hence in the matrix element (124):

$$A_{nn'} = -\frac{F_0}{2}\left(\frac{2\kappa}{l}\right)^{1/2} \int_{-l/2}^{+l/2} \sin k_n x \, e^{-\kappa|x|} x dx. = -\frac{F_0}{2i}\left(\frac{2\kappa}{l}\right)^{1/2} \left(\int_0^{l/2} e^{(ik_n-\kappa)x} x dx - \int_0^{l/2} e^{-(ik_n+\kappa)x} x dx \right). \tag{6.129}$$

These two integrals may be readily worked out by parts. Taking into account that due to the condition (126), their upper limits may be extended to ∞, the result is

$$A_{nn'} = -\left(\frac{2\kappa}{l}\right)^{1/2} F_0 \frac{2k_n \kappa}{\left(k_n^2 + \kappa^2\right)^2}. \tag{6.130}$$

Note that the matrix element is a smooth function of k_n (and hence of E_n), so an important condition of the Golden Rule, the virtual constancy of $A_{nn'}$ on the interval $\Delta E_n \sim \hbar\Gamma \ll E_n$, is satisfied. So, the general Eq. (111) is reduced, for our problem, to the following expression:

$$\Gamma = \frac{2\pi}{\hbar}\left[\left(\frac{2\kappa}{l}\right)^{1/2} F_0 \frac{2k_n\kappa}{(k_n^2+\kappa^2)^2}\right]^2 \frac{lm}{2\pi\hbar^2 k_n} \equiv \frac{8F_0^2 m k_n \kappa^3}{\hbar^3 (k_n^2+\kappa^2)^4}, \tag{6.131}$$

which is independent of the artificially introduced l – thus justifying its use.

Note that due to the above definitions of k_n and κ, the expression in the parentheses in the denominator of the last expression does not depend on the potential well's "weight" $\mathcal{W}$, and is a function of only the excitation frequency ω (and the particle's mass):

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[40] The normalization to infinite volume, by using Eq. (4.263), is also possible, but physically less transparent.

$$\frac{\hbar^2 \left(k_n^2 + \kappa^2 \right)}{2m} = E_n - E_{n'} = \hbar\omega. \tag{6.132}$$

As a result, Eq. (131) may be recast simply as

$$\hbar\Gamma = \frac{F_0^2 \mathcal{W}^3 k_n}{2(\hbar\omega)^4}. \tag{6.133}$$

What is hidden here is that k_n, defined by Eq. (125) with $E_n = E_{n'} + \hbar\omega$, is a function of the external force's frequency, changing as $\omega^{1/2}$ at $\omega \gg \omega_{min}$ (so Γ drops as $\omega^{-7/2}$ at $\omega \to \infty$), and as $(\omega - \omega_{min})^{1/2}$ when ω approaches the "red boundary" (121) of the ionization effect, so $\Gamma \propto (\omega - \omega_{min})^{1/2} \to 0$ in that limit as well.

A conceptually very similar but a bit more involved analysis of this effect in a more realistic 3D case, namely the hydrogen atom's ionization by an optical wave, is left for the reader's exercise.

6.7. Golden Rule for step-like perturbations

Now let us reuse some of our results for a perturbation being turned on at $t = 0$, but after that time-independent:

$$\hat{H}^{(1)}(t) = \begin{cases} 0, & \text{for } t < 0, \\ \hat{H} = \text{const}, & \text{for } t \geq 0. \end{cases} \tag{6.134}$$

A superficial comparison of this equality and the former Eq. (86) seems to indicate that we may use all our previous results, taking $\omega = 0$ and replacing $\hat{A} + \hat{A}^\dagger$ with $\hat{H}^{(1)}$. However, that conclusion (which would give us a wrong factor of 2 in the result) does not take into account the fact that when analyzing both the two-level approximation in Sec. 5 and the Golden Rule in Sec. 6, we have dropped the second (non-resonant) term in Eq. (90). In our current case (134), with $\omega = 0$, there is no such difference between these terms. This is why it is more prudent to use the general Eq. (84),

$$i\hbar \dot{a}_n = \sum_{n'} a_{n'} H_{nn'} e^{i\omega_{nn'}t}, \tag{6.135}$$

in which the matrix element of the perturbation is now time-independent at $t > 0$. We see that it is formally equivalent to Eq. (88) with only the first (resonant) term kept, provided that we make the following replacements:

$$\hat{A} \to \hat{H}, \quad \Delta_{nn'} \equiv \omega - \omega_{nn'} \to -\omega_{nn'}. \tag{6.136}$$

Let us use this equivalency to consider the results of coupling between a discrete-energy state n', to which the particle is initially placed, and a dense group of states with a quasi-continuum spectrum, in the same energy range. Figure 11a shows an example of such a system: a particle is initially (say, at $t = 0$) placed into a potential well separated by a penetrable potential barrier from a formally infinite region with a continuous energy spectrum. Let me hope that the physical discussion in the last section makes the outcome of such an experiment evident: the particle will gradually and irreversibly tunnel out of the well, so the probability $W_{n'}(t)$ of its still residing in the well will decay in accordance with Eq. (114). The rate of this decay may be found by making the replacements (136) in Eq. (111):

$$\Gamma = \frac{2\pi}{\hbar} \left| H_{nn'} \right|^2 \rho_n, \tag{6.137}$$

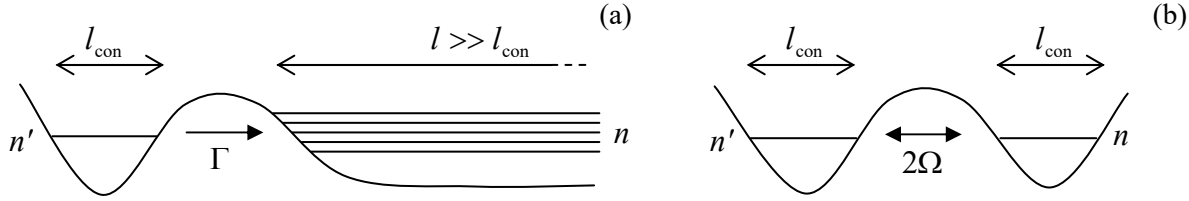where the states n and n' now have virtually the same energy.[41]

Fig. 6.11. Tunneling from a discrete-energy state n': (a) to a state continuum, and (b) to another discrete-energy state n.

It is very informative to compare this result, semi-quantitatively, with Eq. (105) for a symmetric ($E_n = E_{n'}$) system of two potential wells separated by a similar potential barrier – see Fig. 11b. For the symmetric case, i.e. $\xi = 0$, Eq. (105) is reduced to simply

$$\Omega = \frac{1}{\hbar} \left| H_{nn'} \right|_{con}. \tag{6.138}$$

Here I have used the index "con" (from "confinement") to emphasize that this matrix element is somewhat different from the one participating in Eq. (137), even if the potential barriers are similar. Indeed, in the latter case, the matrix element,

$$H_{nn'} \equiv \left\langle n \middle| \hat{H} \middle| n' \right\rangle = \int \psi_{n'}^* \hat{H} \psi_n dx, \tag{6.139}$$

has to be calculated for two wavefunctions ψ_n and $\psi_{n'}$ confined to spatial intervals of the same scale l_{con}, while in Eq. (137), the wavefunctions ψ_n are extended over a much larger distance $l \gg l_{con}$ – see Fig. 11. As Eq. (128) tells us, in the 1D model this means an additional small factor of the order of $(l_{con}/l)^{1/2}$. Now using Eq. (128) as a crude but suitable model for the final-state wavefunctions, we arrive at the following estimate, which is independent of the artificially introduced length l:

$$\hbar\Gamma \sim 2\pi \left| H_{nn'} \right|_{con}^2 \frac{l_{con}}{l} \rho_n \sim 2\pi \left| H_{nn'} \right|_{con}^2 \frac{l_{con}}{l} \frac{lm}{2\pi\hbar^2 k_n} \sim \frac{\left| H_{nn'} \right|_{con}^2}{\Delta E_{n'}} \equiv \frac{(\hbar\Omega)^2}{\Delta E_{n'}}, \tag{6.140}$$

where $\Delta E_{n'} \sim \hbar^2/ml_{con}^2$ is the scale of the distances between the adjacent eigenenergies of the particle in an unperturbed potential well. Since the condition of validity of Eq. (138) is $\hbar\Omega \ll \Delta E_{n'}$, we see that

$$\hbar\Gamma \sim \frac{\hbar\Omega}{\Delta E_n} \hbar\Omega \ll \hbar\Omega.. \tag{6.141}$$

This (sufficiently general[42]) perturbative result confirms the conclusion of a more particular analysis carried out at the end of Sec. 2.6: the rate of the (irreversible) quantum tunneling into a state continuum is always *much lower* than the frequency of (reversible) quantum oscillations between

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[41] The condition of validity of Eq. (137) is again given by Eq. (117), just with $\omega = 0$ in the upper limit for Γ.
[42] It is straightforward to verify that the estimate (141) is valid for similar problems of any spatial dimensionality, not just for the 1D case we have analyzed.

discrete states separated with the same potential barrier – at least for the case when both are much lower than $\Delta E_n'/\hbar$, so the perturbation theory is valid. A very handwaving interpretation of this result is that the particle performs the quantum oscillations between the confined state in the well and the space-extended states behind the barrier many times before finally "deciding to perform" an irreversible transition into the unconfined continuum. This qualitative picture is consistent with experimentally observable effects of dispersive electromagnetic environments on electron tunneling.[43]

Let me conclude this section (and this chapter) with the application of Eq. (137) to a very important case that will provide a smooth transition to the next chapter's topic. Consider a *composite* system consisting of two *component* systems, *a* and *b*, with the energy spectra sketched in Fig. 12.
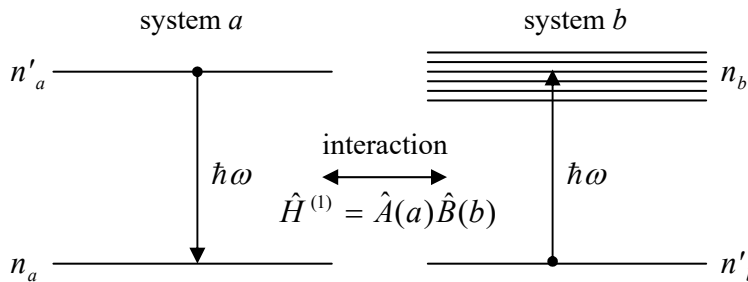

Fig. 6.12. Energy relaxation in system *a* due to its weak coupling to system *b* (which serves as the environment of *a*).

Let the systems be completely independent initially. The independence means that in the absence of their coupling, the total Hamiltonian of the system may be represented as a sum of two operators:

$$\hat{H}^{(0)} = \hat{H}_a(a) + \hat{H}_b(b), \tag{6.142}$$

where arguments *a* and *b* symbolize the non-overlapping sets of the degrees of freedom of the two systems. Such operators, belonging to their individual, different Hilbert spaces, naturally commute. Similarly, the eigenkets of the system may be naturally factored as

Direct
product

$$\boxed{|n\rangle = |n_a\rangle \otimes |n_b\rangle .} \tag{6.143}$$

The *direct product* sign $\otimes$ is used here (and below) to denote the formation of a joint ket-vector from the kets of the independent systems, belonging to different Hilbert spaces. Evidently, the order of operands in such a product may be changed at will. As a result, its eigenenergies separate into a sum, just as the Hamiltonian (142) does:

$$\hat{H}^{(0)}|n\rangle = \left(\hat{H}_a + \hat{H}_b\right)|n_a\rangle \otimes |n_b\rangle \equiv \left(\hat{H}_a|n_a\rangle\right)\otimes |n_b\rangle + \left(\hat{H}_b|n_b\rangle\right)\otimes |n_a\rangle = \left(E_{na} + E_{nb}\right)|n\rangle . \tag{6.144}$$

In such composite systems, the relatively weak interaction of its components may be usually represented as a product of two Hermitian operators, each depending only on the degrees of freedom of one component system:

$$\hat{H}^{(1)} = \hat{A}(a)\hat{B}(b) . \tag{6.145}$$

A very common example of such an interaction is the electric-dipole interaction between an atomic-scale system (with a linear size of the order of the Bohr radius $r_B \sim 10^{-10}$ m) and the electromagnetic field at optical frequencies $\omega \sim 10^{16}$ s^{-1}, with the wavelength $\lambda = 2\pi c/\omega \sim 10^{-6}$ m $\gg r_B$:

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[43] See, e.g., P. Delsing *et al.*, *Phys. Rev. Lett.* **63**, 1180 (1989).

$$\hat{H}^{(1)} = -\hat{\mathbf{d}} \cdot \hat{\boldsymbol{\mathscr{E}}}, \qquad \text{with} \quad \hat{\mathbf{d}} \equiv \sum_k q_k \hat{\mathbf{r}}_k, \tag{6.146}$$

where the dipole electric moment $\mathbf{d}$ depends only on the positions $\mathbf{r}_k$ of the charged particles (numbered with index k) of the atomic system, while the electric field $\boldsymbol{\mathscr{E}}$ is a function of only the electromagnetic field's degrees of freedom – to be discussed in Chapter 9 below.

Returning to the general situation shown in Fig. 12, if the component system a was initially in an excited state n'_a, the interaction (145), turned on at some moment of time, may bring it into another discrete state n_a of lower energy – for example, the ground state. In the process of this transition, the released energy, in the form of an energy quantum

$$\hbar\omega \equiv E_{n'a} - E_{na}, \tag{6.147}$$

is picked up by system b:

$$E_{nb} = E_{n'b} + \hbar\omega \equiv E_{n'b} + \left(E_{n'a} - E_{na} \right), \tag{6.148}$$

so the total energy $E = E_a + E_b$ of the system does not change. (If the states n_a and n'_b are the ground states of the component systems, as they are in most applications of this analysis, and we take the ground state energy $E_g = E_{na} + E_{n'b}$ of the composite system for the reference, then Eq. (148) gives merely $E_{nb} = E_{n'a}$.) If the final state n_b of system b is inside a state group with a quasi-continuous energy spectrum (Fig. 12), the process has the exponential character (114)[44] and may be interpreted as the effect of *energy relaxation* of system a, with the released energy quantum $\hbar\omega$ *absorbed* by system b.

If the relaxation rate Γ is sufficiently low, it may be described by the Golden Rule (137). Since the perturbation (145) does not depend on time explicitly, and the total energy E does not change, this relation, with the account of Eqs. (143) and (145), takes the form

$$\Gamma = \frac{2\pi}{\hbar} |A_{nn'}|^2 |B_{nn'}|^2 \rho_n, \quad \text{where} \quad A_{nn'} \equiv \left\langle n_a \left| \hat{A} \right| n'_a \right\rangle, \quad \text{and} \quad B_{nn'} = \left\langle n_b \left| \hat{B} \right| n'_b \right\rangle, \tag{6.149}$$

Golden Rule for coupled systems

where ρ_n is the density of the final states of system b at the relevant energy (147).[45] In particular, Eq. (149), with the dipole Hamiltonian (146), will enable us to readily calculate, in Chapter 9, the natural linewidth of atomic electric-dipole transitions.

Instead, I will now proceed to a general discussion of the effects of quantum systems' interaction with their environment, toward which the situation shown in Fig. 12 provides a clear conceptual path. Indeed, in this case the transition from the Hamiltonian (and hence reversible) quantum dynamics of the whole composite system $a + b$ to the Golden-Rule-governed (and hence irreversible) dynamics of system a has been achieved essentially by following this component system alone, i.e. ignoring the details of the exact state of system b. (As was argued in the previous section, the quasi-continuous spectrum of the latter system essentially requires it to have a large spatial size, so it may be legitimately called the *environment* of the "open" system a.) This is exactly the approach that will be pursued in the next chapter.

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[44] This process is *spontaneous*: it starts as soon as either the interaction (145) has been turned on or (if it had been already on) as soon as the system a is placed into the excited state n'_a.

[45] Note that these partial matrix elements may be calculated in the Heisenberg picture as well, because due to the general Eq. (4.149) and the energy balance (147), the additional time dependences of these elements would be proportional to $\exp\{\pm i\omega t\}$, and cancel at their multiplication.

6.8. Exercise problems

6.1. Use Eq. (6.14) of the lecture notes to prove the following general form of the Hellmann-Feynman theorem:[46]

$$\frac{\partial E_n}{\partial \lambda} = \left\langle n \left| \frac{\partial \hat{H}}{\partial \lambda} \right| n \right\rangle,$$

where λ is an arbitrary c-number parameter.

6.2. Establish a relation between Eq. (16) and the result of the classical theory of weakly anharmonic ("nonlinear") oscillations at negligible damping.

Hint: You may like to use N. Bohr's reasoning that was discussed in Problem 1.1.

6.3. An additional weak time-independent force F is exerted on a 1D particle that had been placed into a hard-wall potential well

$$U(x) = \begin{cases} 0, & \text{for } 0 < x < a, \\ +\infty, & \text{otherwise.} \end{cases}$$

Calculate, sketch, and discuss the 1st-order perturbation of its ground-state wavefunction.

6.4. A time-independent force $\mathbf{F} = \mu(\mathbf{n}_x y + \mathbf{n}_y x)$, where μ is a small constant, is applied to a 3D isotropic harmonic oscillator of mass m and frequency ω_0, located at the origin. Calculate, in the first order of the perturbation theory, the effect of the force upon the ground-state energy of the oscillator and its lowest excited energy level. How small should the constant μ be for your results to be quantitatively correct?

6.5. A 1D particle of mass m is localized at a narrow potential well that may be approximated with a delta function:

$$U(x) = -\mathcal{W}\delta(x), \qquad \text{with } \mathcal{W} > 0.$$

Calculate the change of its ground state energy by an additional weak time-independent force F, in the first non-vanishing approximation of the perturbation theory. Discuss the limits of validity of this result, taking into account that at $F \neq 0$, the localized state of the particle is metastable.

6.6. Use Eq. (16) to calculate the eigenvalues of the operator $\hat{L}^2$, in the limit $|m| \approx l \gg 1$, by purely wave-mechanical means.

Hint: Try the following substitution: $\Theta(\theta) = f(\theta)/\sin^{1/2}\theta$.

6.7. In the lowest non-vanishing order of the perturbation theory, calculate the shift of the ground-state energy of an electrically charged spherical rotor (i.e. a particle of mass m, free to move over a spherical surface of radius R) due to a weak uniform time-independent electric field $\mathcal{E}$.

6.8. Use the perturbation theory to evaluate the effect of a time-independent uniform electric field $\mathcal{E}$ on the ground state energy E_g of a hydrogen atom. In particular:

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[46] As a reminder, proof of its wave-mechanics form was the task of Problem 1.7.

(i) calculate the 2nd-order shift of E_g, neglecting the extended unperturbed states with $E > 0$, and bring the result to the simplest analytical form you can,

(ii) find the lower and the upper bounds on the shift, and

(iii) discuss the simplest experimental manifestation of this *quadratic Stark effect*.

6.9. A particle of mass m, with electric charge q, is in its ground s-state with a given energy $E_g < 0$, being localized by a very-short-range, spherically symmetric potential well. Calculate its static electric polarizability.

6.10. In some atoms, the effect of nuclear charge screening by electrons on the motion of each of them may be reasonably well approximated by the replacement of the Coulomb potential (3.190), $U = -C/r$, with the so-called *Hulthén potential*

$$U = -\frac{C/a}{\exp\{r/a\} - 1} \to -C \times \begin{cases} 1/r, & \text{for } r \ll a, \\ \exp\{-r/a\}/a, & \text{for } a \ll r. \end{cases}$$

Assuming that the effective screening radius a is much larger than $r_0 \equiv \hbar^2/mC$, use the perturbation theory to calculate the energy spectrum of a single particle of mass m, moving in this potential, in the lowest order needed to lift the l-degeneracy of the energy levels.

6.11. In the lowest non-vanishing order of the perturbation theory, calculate the correction to energies of the ground state and all lowest excited states of a hydrogen-like atom/ion, due to the electron's penetration into the nucleus, by modeling it the latter a spinless, uniformly charged sphere of radius $R \ll r_B/Z$.

6.12. A particle of mass m is placed inside a hard-wall ellipsoid whose surface is described by the equation

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2} = 1, \qquad \text{with } b = (1 + \varepsilon)a, \quad |\varepsilon| \ll 1.$$

Calculate its ground-state energy in the 1st order in the small parameter ε, and interpret the result.

6.13. Prove that the relativistic correction operator (48) indeed has only diagonal matrix elements in the basis of unperturbed Bohr atom states (3.200).

6.14. Calculate the lowest-order relativistic correction to the ground-state energy of a 1D harmonic oscillator.

6.15. Use the perturbation theory to calculate the contribution to the magnetic susceptibility χ_m of a dilute gas, that is due to the orbital motion of a single electron inside each gas particle. Spell out your result for a spherically symmetric ground state of the electron, and give an estimate of the magnitude of this *orbital susceptibility*.

6.16. A certain energy level degeneracy is not lifted in the 1st order of the stationary perturbation theory. Calculate its lifting in the 2nd order of the theory. Apply the result to a planar rotor of mass m and radius R, with electric charge q, placed into a weak, uniform, time-independent electric field $\mathscr{E}$.

6.17.[*] The Hamiltonian of a quantum system is slowly changed over time.

(i) Develop a theory of quantum transitions in the system, and spell out its result in the 1st approximation in the speed of the change.

(ii) Use this approximation to calculate the probability that a finite-time pulse of a slowly changing force $F(t)$ drives a 1D harmonic oscillator, initially in its ground state, into an excited state.

(iii) Compare the last result with the exact one.

6.18. Use the single-particle model to calculate the complex electric permittivity $\varepsilon(\omega)$ of a dilute gas of similar atoms, due to their induced electric polarization by a weak external ac field, for a field frequency ω very close to one of the quantum transition frequencies $\omega_{nn'}$. Based on the result, calculate and estimate the absorption cross-section of each atom.

Hint: In the single-particle model, the atom's properties are determined by Z similar, non-interacting electrons, each moving in a similar static attracting potential, generally different from the Coulomb one, because it is contributed not only by the nucleus but also by other electrons.

6.19. Use the solution of the previous problem to generalize the expression for the London dispersion force between two atoms (whose calculation in the harmonic oscillator model was the subject of Problems 3.20 and 5.20) to the single-particle model with an arbitrary energy spectrum.

6.20. Use the solution of the previous problem to calculate the potential energy of the interaction of two hydrogen atoms, both in their ground state, separated by distance $r \gg r_B$.

6.21. In a certain quantum system, distances between the three lowest energy levels are slightly different – see the figure on the right ($|\xi| \ll \omega_{1,2}$). Assuming that the involved matrix elements of the perturbation Hamiltonian are known and are all proportional to the external ac field's amplitude, find the time necessary to populate the first excited level almost completely (with a given precision $\varepsilon \ll 1$), by using the Rabi oscillation effect, if at $t = 0$, the system is in its ground state. Spell out your result for a weakly anharmonic 1D oscillator.

E_2 ———

$\hbar\omega_2 = \hbar(\omega_1 + \xi)$

E_1 ———

$\hbar\omega_1$

E_0 ———
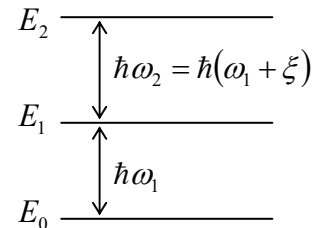
6.22.[*] Analyze the possibility of a slow transfer of a system from one of its energy levels to another one (in the figure on the right, from level 1 to level 3), by using the scheme shown in that figure, in which the monochromatic external excitation amplitudes A_+ and A_- may be slowly changed at will.

E_2 ———

A_+ $\hbar\omega_+$ A_- $\hbar\omega_-$

E_3

E_1 ———
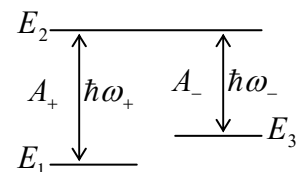
6.23. A weak external force pulse $F(t)$, of a finite time duration, is applied to the particle in a system with a discrete energy spectrum, which initially was in its ground state.

(i) Derive, in the lowest non-vanishing order of the perturbation theory, a formula for the probability that the pulse drives the particle into its lowest excited state.

(ii) Specify this formula for a 1D harmonic oscillator and compare the result with the exact solution of the problem.

(iii) Spell out the perturbative result for the Gaussian-shaped waveform $F(t) = F_0\exp\{-t^2/\tau^2\}$ and analyze its dependence on the scale τ of the pulse duration.

6.24. A spatially uniform but time-dependent external electric field $\mathscr{E}(t)$ is applied, starting from $t = 0$, to a charged planar rotor, initially in its ground state.

(i) Calculate, in the lowest non-vanishing order in the field's strength, the probability that by a certain time $t > 0$, the rotor is in its mth excited state.

(ii) Spell out and analyze your results for a constant-magnitude field rotating, with a constant angular velocity ω, within the rotor's plane.

(iii) Do the same for a monochromatic field of frequency ω, with a fixed direction.

6.25. A heavy relativistic particle, with electric charge $q = Ze$, flies by a hydrogen atom, initially in its ground state, with an impact parameter b within the range $r_B \ll b \ll r_B/\alpha$, where $\alpha \approx 1/137$ is the fine structure constant. Calculate the total probability of the atom's transition to one of its lowest excited states.

6.26. Develop a general theory of quantum excitations of the higher levels of a discrete-spectrum system, initially in the ground state, by a weak time-dependent perturbation, up to the 2nd order. Spell out and discuss the result for the case of monochromatic excitation, with a nearly perfect tuning of its frequency ω to *the half* of a certain quantum transition frequency $\omega_{n0} \equiv (E_n - E_0)/\hbar$.

6.27. A particle of mass m is initially in a localized ground state, with energy $E_g < 0$, of a very-short-range, spherically symmetric potential well. Calculate the rate of its delocalization by an applied classical force $\mathbf{F}(t) = \mathbf{n}F_0\cos\omega t$ with a time-independent direction $\mathbf{n}$.

6.28.[*] Calculate the rate of ionization of a hydrogen atom, initially in its ground state, by a classical, linearly polarized electromagnetic wave with an electric field's amplitude $\mathscr{E}_0$, and a frequency ω within the range

$$\frac{\hbar}{m_e r_B^2} \ll \omega \ll \frac{c}{r_B}.$$

Recast your result in terms of the cross-section of electromagnetic wave absorption. Discuss briefly what changes of the theory would be necessary if either of the above conditions had been violated.

6.29.[*] Use the quantum-mechanical Golden Rule to derive the general expression for the electric current I through a weak tunnel junction between two conductors, biased with dc voltage V, treating the conductors as degenerate Fermi gases of electrons with negligible direct interaction. Simplify the result in the low-voltage limit.

Hint: The electric current flowing through a weak tunnel junction is so low that it does not substantially perturb the electron states inside each conductor.

6.30.[*] Generalize the result of the previous problem to the case when a weak tunnel junction is biased with voltage $V(t) = V_0 + A\cos\omega t$, with $\hbar\omega$ generally comparable with eV_0 and eA.

6.31.[*] Use the quantum-mechanical Golden Rule to derive the Landau-Zener formula (2.257).