RANDOM MATRIX LINE SHAPE THEORY WITH APPLICATIONS TO LÉVY STATISTICS*

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A model system of a bright state coupled to a manifold of dark states is analyzed with regard to the width distributions of the dark manifold induced in the bright state. Independent box shaped distributions are assumed for the energy distributions, the coupling distributions and the dark level width-distributions. The width distributions induced via the couplings from the dark levels into the bright state can be expressed in terms of Lévy functions in the limit of a sparse level density which relates to anomalous long-time relaxations of the state selected survival probabilities.

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1. Introduction

Equilibrium statistical mechanics is based on two postulates: 1. The long time average of an observable of a thermodynamic system equals the ensemble average, and 2. All microstates compatible with the macroscopic constraints of a thermodynamic system have equal *a priori* probability [1]. For simple systems like gases or fluids the long time average is established on a time scale short compared to the timescale for typical time resolved measurements. For complex systems like proteins this is not necessarily so. For instance the rebinding kinetics of CO in myoglobin after a flash induced dissociation can span at low temperatures over 12 orders of magnitude from picoseconds to seconds or days. This process is described by dispersive kinetics [2]. It implies the existence of an overlay of many systems with different activation energies. The ensemble of such systems (proteins) may be equilibrated in terms of the temperature but not with regard to their

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detailed microscopic structure. There may be water molecules in different H-bonding positions, titratable groups may differ in their protonation state, and flexible groups may be frozen in slightly different arrangements. Such an ensemble can be characterized by an ensemble of Hamiltonians, which differ in their microstructure and as a result in microscopic parameters, such as eigenvalues, interactions, lifetimes, *etc*. There is a certain amount of lack of knowledge about the detailed structure of every element of the ensemble. Models can characterize the range and probability distribution of these parameters. Since the Hamiltonians contain elements of randomness we use the term "Random Matrix Theory" [3]. The ensemble becomes a grand canonical ensemble in the sense that each representative system is part of a canonical ensemble. But the different canonical ensembles are allowed to differ for instance in the number of water molecules and consequently in their structure, energy, *etc*. The difference to an equilibrium grand canonical ensemble lies in the fact that the particle (water) exchange is slow compared to the time scale of the measurements. Only at high temperatures, typically above the melting point of ice, the diffusive exchange between the solvent and a protein becomes so fast, that the dispersive kinetics approaches a normal kinetics and the inhomogeneous grand ensemble becomes a normal grand ensemble for which the two postulates stated above prevail.

In this paper we concentrate on the nonergodic limit. We analyze an ensemble of model Hamiltonians, each consisting of a bright state coupled to a manifold of dark states. The dark states are thought to be diagonalized in the absence of the bright state, so that they do not interact directly among each other [4]. We shall analyze the line shape as a function of the probability distribution of the energies E_l of the dark states l, the distribution of the interactions v_{sl} between the bright and the dark states and the distribution of the widths γ_l of the dark states in relation to the width γ_0 of the bright state. Related results have been published in the context of intermolecular vibrational relaxations [5,6]. To simplify the model we assume that all three random variables E_l, v_{sl} and γ_l are independent and that the distribution functions are always box shaped. We will find for the limit of a low density of dark states Lévy distributions for the widths, whereby the Lévy index depends on the location of the width of the bright state relative to the location of the box for the dark-state width distribution. Possible applications to stochastic processes in the time domain are also discussed.

2. Hamiltonian and line shape function

We consider a 'bright' state $|s\rangle$ with energy E_s, which couples to L 'dark' states $|l\rangle$, with energies E_l, $l = 1, 2, \dots L$ and finite lifetimes due to imaginary parts $-i\gamma_0$ and $-i\gamma_l$ of the complex energies,

$$H = |s\rangle(E_s - i\gamma_0)\langle s| + \sum_{l=1}^{L} |l\rangle(E_l - i\gamma_l)\langle l| + \sum_{l=1}^{L}(|s\rangle v_{sl}\langle l| + |l\rangle v_{ls}\langle s|)\,. \quad (2.1)$$

We introduce a statistical ensemble for the matrix elements of H with the combined probability density

$$P(E_1, \ldots, E_L, v_{s1}, \ldots, v_{sL}, \gamma_1, ..., \gamma_L) = \prod_{l=1}^{L} f(E_l)\, g(v_{sl}) h(\gamma_l)\,, \quad (2.2)$$

with the uniform probability density for the dark states,

$$f(E) = \begin{cases} 1/(2\Delta) & \text{if } |E - E_s| \le \Delta \\ 0 & \text{if } |E - E_s| \ge \Delta \end{cases}\,, \quad (2.3)$$

and the mean density of states

$$\rho_0 = \frac{N}{2\Delta}\,. \quad (2.4)$$

The functions $g(v_{sl})$ and $h(v_{sl})$ will be specified later. We further express the absorption line shape function $L(E)$ for nonabsorbing dark states in terms of the Green's function

$$G_{ss} = [E_+ - E_s + i\gamma_0 - R(E)]^{-1}\,, \quad (2.5)$$

as

$$L(E) = -\pi^{-1}\mathrm{Im}\{G_{ss}\}\,, \quad (2.6)$$

with the level shift

$$R(E) = \sum_{l=1}^{L} \frac{|v_{sl}|^2}{E_+ - E_l + i\gamma_l}\,, \quad (2.7)$$

and

$$E_+ = E + i\varepsilon; \qquad \varepsilon \to 0\,. \quad (2.8)$$

Following the derivation of Eq. (3.12) in Ref. [4], we consider a Poisson distribution of the number of dark states. The ensemble line shape function (ELSF),

$$\overline{L}(E) = \sum_{L=0}^{\infty} e^{-N}\frac{N^L}{L!}\langle L(E)\rangle\,, \quad (2.9)$$

then becomes

$$\overline{L}(E) = \pi^{-1}\mathrm{Re}\left(\int_0^\infty \exp\left\{ik[E_+ - E_s + i\gamma_0 - S(E,k)]\right\}dk\right) \qquad (2.10)$$

with the "shift function"

$$S(E,k) = ik^{-1}N\left\langle\int_{-\infty}^{\infty}\left[\exp\left(-ik\frac{v^2}{E_+ - E_l + i\gamma_l}\right) - 1\right]f(E_l)dE_l\right\rangle_{v,\gamma}, \qquad (2.11)$$

where the angular brackets indicate average formation with respect to the ensemble

$$\langle\ldots\rangle = \int\ldots\int\ldots\Pi_{l=1}^N f(E_l)g(v_{sl})h(\gamma_l)dE_l dv_{sl}d\gamma_l\,, \qquad (2.12)$$

and

$$\langle\ldots\rangle_{v,\gamma} = \int\ldots g(v)h(\gamma_l)dvd\gamma_l\,. \qquad (2.13)$$

Here it is also instructive to perform the expansion

$$S(E,k) = ik^{-1}N\sum_{j=1}^{\infty}\frac{(-ik)^j}{j!}\left\langle v^{2j}\right\rangle_v\left\langle\int_{-\infty}^{\infty}(E_+ - E_l + i\gamma_l)^{-j}f(E_l)dE_l\right\rangle_\gamma, \qquad (2.14)$$

considering the quasidegenerate limit of broad dark levels

$$\sqrt{N}|v_{sl}|, \qquad \Delta \ll \gamma_l\,. \qquad (2.15)$$

In this limit we can neglect in Eq. (2.14) the energy part $E_+ - E_l$ in the denominator, and see that terms of second and higher order under the integral are small compared to the first order term. Keeping only the latter we obtain a constant shift function with a negative imaginary part only:

$$S(E,k) = -i\left\langle\sum_{l=1}^{L}\frac{v^2}{\gamma_l}\right\rangle_{\gamma,v} = -iN\left\langle v^2\right\rangle_v\langle 1/\gamma_l\rangle_\gamma\,. \qquad (2.16)$$

Hence we get from (2.10)

$$\overline{L}(E) = \pi^{-1}\mathrm{Re}\left(\int_0^\infty \exp\left[ik(E_+ - E_s + i\gamma_0) - k\langle v^2\rangle N\langle 1/\gamma_l\rangle\right]dk\right), \qquad (2.17)$$

and the ELSF becomes the Lorentzian

$$\overline{L}(E) = \frac{\Gamma/(2\pi)}{(E_+ - E_s)^2 + \Gamma^2/4}\,, \tag{2.18}$$

with the width being broadened relative to the unperturbed part $2\gamma_0$ by twice the negative imaginary part of the shift function,

$$\Gamma \equiv \Gamma_d = 2\gamma_0 + 2\langle v^2 \rangle N \langle 1/\gamma_l \rangle\,. \tag{2.19}$$

In the other limit of an unbounded uniform probability density $f(E_l)$ one has to take the limits $N, \Delta \to \infty$ in (2.3) at a fixed mean density of the l-states $\rho_0 \equiv N/(2\,\Delta)$. In this limit we obtain from (2.14)

$$S(E,k) = ik^{-1}\rho_0 \sum_{j=1}^{\infty} \frac{(-ik)^j}{j!} \left\langle v^{2j} \right\rangle_v \left\langle \int_{-\infty}^{\infty} (E_+ - E_l + i\gamma_l)^{-j} dE_l \right\rangle_\gamma . \tag{2.20}$$

Here terms with $j \geq 2$ vanish, as can be verified using Cauchy's theorem after the closure of the integration path in the upper half plane. Performing the integration of the remaining ($j = 1$)-term results again in a constant shift function

$$S(E,k) = -i\pi\rho_0\langle v^2 \rangle\,, \tag{2.21}$$

which gives rise for the Lorentzian ELSF (2.18), now with the width

$$\Gamma \equiv \Gamma_u = 2\gamma_0 + 2\pi\rho_0\langle v^2 \rangle\,. \tag{2.22}$$

This result holds for all coupling distributions with finite moments. That means, we found that the line shape function can become a Lorentzian for a large class of systems, which describe an inhomogeneously distributed noninteracting ensemble. More detailed information about the nature of the underlying coupling- and width distributions can be obtained from time resolved experiments.

3. Widths distributions

Here we evaluate the distribution of the homogeneous width, which is induced in the bright state due to the coupling to the dark states. Confining to leading order perturbation, we take the negative imaginary part of the complex second order energy

$$\tilde{E}_s - i\tilde{\gamma}_s = E_s - i\gamma_0 + \sum_{l=1}^{N} \frac{v_{sl}^2}{E_s - i\gamma_0 - E_l + i\gamma_l} \tag{3.1}$$

as the width of the bright state

$$\tilde{\gamma}_s = \gamma_0 + \sum_{l=1}^{N} \lambda_l \tag{3.2}$$

with

$$\lambda_l = \frac{v_{sl}^2(\gamma_l - \gamma_0)}{(E_l - E_s)^2 + (\gamma_l - \gamma_0)^2} \,. \tag{3.3}$$

Considering again the quasidegenerate limit, we obtain for a single dark level the second order s-level width $\tilde{\gamma}_0$ as $\gamma_0 + v_{sl}^2/(\gamma_l - \gamma_0)$, which we denote as γ, for simplicity. For a positive constant $\gamma_l - \gamma_0 \equiv \gamma_1$, its distribution $N(\gamma)$ vanishes for γ values below γ_0. For $\gamma \geq \gamma_0$ it is given by

$$N(\gamma) = g(v_{sl})|dv_{sl}/d\gamma| = \frac{\sqrt{\gamma_1}}{2}(\gamma - \gamma_0)^{-1/2} g(\sqrt{\gamma_1(\gamma - \gamma_0)}) \,. \tag{3.4}$$

For a Gaussian coupling distribution with zero mean and variance $\overline{v}$, the Porter–Thomas distribution, which is also known from nuclear physics [7], follows

$$N(\gamma) = \frac{\sqrt{\gamma_1}}{2\sqrt{2\pi}\overline{v}}(\gamma - \gamma_0)^{-1/2} \exp\left[-\frac{\gamma_1(\gamma - \gamma_0)}{2\overline{v}^2}\right] . \tag{3.5}$$

For many l-states with equal constant widths $\gamma_l = \gamma_1 + \gamma_0$ the induced second-order width is

$$\gamma - \gamma_0 = \gamma_1^{-1} \sum_{l=1}^{N} v_{sl}^2 \,. \tag{3.6}$$

If the coupling distributions have finite variances, the central limit theorem applies, and γ is Gaussian distributed with a rms deviation of $\sqrt{N(\langle v^4 \rangle - \langle v^2 \rangle^2)}/\gamma_1$ around the mean value $\gamma_0 + N\langle v^2 \rangle/\gamma_1$, regardless of the coupling distributions.

Next, and most important for this paper, we incorporate the influence of variable energies E_l and widths γ_l upon $N(\gamma)$. Again we refer to the Hamiltonian matrix ensemble (2.12), considering now

$$N(\gamma) = \langle \delta(\gamma - \tilde{\gamma}_s) \rangle \,, \tag{3.7}$$

where the angular brackets indicate the ensemble average (2.12). In this case it is advantageous to consider instead of $N(\gamma)$ its Fourier transform, or its characteristic function

$$Q(\beta) = \int_{-\infty}^{\infty} N(\gamma) \exp(-i\beta\gamma) d\gamma \,. \tag{3.8}$$

Then one retrieves $N(\gamma)$ via the Fourier back-transform of $Q(\beta)$ as

$$N(\gamma) = \frac{1}{2\pi} \int Q(\beta) \exp(i\beta\gamma) d\beta \,. \tag{3.9}$$

After substituting (3.7) for $N(\gamma)$ and integrating over the Delta-function one obtains from Eq. (3.8)

$$Q(\beta) = \langle \exp(-i\beta\tilde{\gamma}_s) \rangle \,. \tag{3.10}$$

Thanks to its exponential structure, and due to the separation of the second order width $\tilde{\gamma}_s$ and the ensemble probability density into equivalent one-level terms, according to the Eqs. (3.2) and (2.12), $Q(\beta)$ factorizes into the s-level part $\exp(-i\beta\gamma_0)$ and the N-th power of the l-level average,

$$\langle \exp(-i\beta\lambda_l) \rangle_l^N \equiv \left\{ 1 - \left\langle \int [1 - \exp(-i\beta\lambda_l)] f(E_l) dE_l \right\rangle_{v,\gamma} \right\}^N \tag{3.11}$$

with the one-level average formation

$$\langle \ldots \rangle_l = \int \ldots f(E_l) g(v) h(\gamma_l) dv d\gamma_l \,. \tag{3.12}$$

Choosing for the probability density of the l-state energies, $f(E_l)$, again the uniform density (2.3) with the unbounded limit $N, \Delta \to \infty$ at the given mean density of states ρ_0, we may write $Q(\beta)$ as a power function with an infinite exponent,

$$Q(\beta) = \exp(-i\beta\gamma_0) \lim_{N\to\infty} \left\{ 1 - \frac{\rho_0}{N} \left\langle \int [1 - \exp(-i\beta\lambda_l)] dE_l \right\rangle_{v,\gamma} \right\}^N \,. \tag{3.13}$$

This function represents an exponential function, yielding for $Q(\beta)$ the result [5]

$$Q(\beta) = \exp[-i\beta\gamma_0 - q(\beta)] \,, \tag{3.14}$$

with

$$q(\beta) = \rho_0 \left\langle \int [1 - \exp(-i\beta\lambda_l)] dE_l \right\rangle_{v,\gamma} \,. \tag{3.15}$$

In order to manage here the integrations we express the integrand as

$$i\lambda_l \int_0^\beta \exp(-ix\lambda_l) dx \,, \tag{3.16}$$

and after exchanging the order of integrations we obtain for $q(\beta)$

$$q(\beta) = i\rho_0 \left\langle \int_0^\beta q_1(x)dx \right\rangle_{v,\gamma} \tag{3.17}$$

with

$$q_1(x) = \int \lambda_l \exp(-ix\lambda_l) dE_l \,, \tag{3.18}$$

and with λ_l from (3.3). Substituting here the new integration variable

$$\phi = 2 \arctan\left(\frac{E_l - E_s}{|\gamma_l - \gamma_0|}\right), \tag{3.19}$$

we get for $q_1(x)$ the expression

$$q_1(x) = v^2 \mathrm{sign}(\gamma_l - \gamma_0) \int_{-\pi}^{\pi} \exp\left[-i \frac{xv^2}{\gamma_l - \gamma_0} \cos^2(\phi/2)\right] d\phi/2 \,, \tag{3.20}$$

which we can rewrite as

$$\begin{aligned} q_1(x) = \quad & v^2 \mathrm{sign}(\gamma_l - \gamma_0) \exp\left[-i \frac{xv^2}{2(\gamma_l - \gamma_0)}\right] \\ & \times \left\{ \int_0^\pi \cos\left[\frac{xv^2}{2(\gamma_l - \gamma_0)} \cos\phi\right] d\phi - i \right. \\ & \left. \times \int_0^\pi \sin\left[\frac{xv^2}{2(\gamma_l - \gamma_0)} \cos\phi\right] d\phi \right\}. \end{aligned} \tag{3.21}$$

In this expression, the integral in the first term represents π times the zeroth order Bessel function J_0 with the argument $xv^2/[2(\gamma_l - \gamma_0)]$ [9], whereas the integral in the second term vanishes, because the integrand is an odd function of ϕ with respect to the midpoint $\pi/2$ of the integration interval. Hence we get for $q_1(x)$ the result

$$q_1(x) = \pi v^2 \mathrm{sign}(\gamma_l - \gamma_0) \exp\left[-i \frac{xv^2}{2(\gamma_l - \gamma_0)}\right] J_0 \left[\frac{xv^2}{2(\gamma_l - \gamma_0)}\right] . \tag{3.22}$$

By inserting this into (3.17) and performing the integration over dx, we obtain

$$q(\beta) = 2\pi i \rho_0 \langle |\gamma_l - \gamma_0| \beta_l \Phi(\beta_l) \rangle_{v,\gamma} \,, \tag{3.23}$$

with

$$\beta_l = \beta \frac{v^2}{2(\gamma_l - \gamma_0)}\,, \tag{3.24}$$

and

$$\Phi(\beta_l) = e^{-i\beta_l}[J_0(\beta_l) + iJ_1(\beta_l)]\,. \tag{3.25}$$

Now we further specify the probability densities of the l-level widths and of the bright-dark couplings as the box shaped distributions:

$$h(\gamma_l) = \begin{cases} 1/\Delta\gamma_0 & \text{if } \gamma_1' \le \gamma_l - \gamma_0 \le \gamma_2' \\ 0 & \text{else} \end{cases} \tag{3.26}$$

with the lower and upper boundaries γ_1' and γ_2' taken relative to γ_0, and with

$$g(v) = \begin{cases} 1/(2V) & \text{if } |v| \le V \\ 0 & \text{else} \end{cases}\,, \tag{3.27}$$

which is symmetric relative to the vanishing mean. Then, making use of this symmetry, we obtain from Eq. (3.23)

$$q(\beta) = \frac{2i\pi\rho_0}{V\Delta\gamma_0} \int_{\gamma_0+\gamma_1'}^{\gamma_0+\gamma_2'} \int_0^V |\gamma_l - \gamma_0|\beta_l \Phi(\beta_l) dv\, d\gamma_l\,. \tag{3.28}$$

After exchanging here the sequence of integrations, performing subsequently the integration over γ_l, we get for $q(\beta)$ the closed-form expression (Appendix A)

$$q(\beta) = i\pi\beta \frac{\rho_0 V^2}{5\Delta\gamma_0}[|\gamma_2'|F(\alpha_2) - |\gamma_1'|F(\alpha_1)]\,, \tag{3.29}$$

with

$$\alpha_i = \beta \frac{V^2}{2\gamma_i'}\,, \tag{3.30}$$

where $i = 1, 2$, and

$$F(\alpha) = F_1(\alpha) + F_2(\alpha)\,, \tag{3.31}$$

with

$$F_1(\alpha) = \alpha^{-3/2} \int_0^\alpha \sqrt{y}\phi(y) dy\,, \tag{3.32}$$

and

$$F_2(\alpha) = \alpha \int_\alpha^{(\mathrm{sign}\alpha)\infty} \frac{\Phi(y)}{y^2} dy\,. \tag{3.33}$$

4. Limiting cases

In order to specify the conditions for limiting cases we like to point at a formal analogy between the characteristic function of the homogeneous-width distribution $N(\gamma)$ and the ensemble averaged decay of the population of the perturbed bright-states for the case that they decay independently from each other. This scenario relates to the limit where the coherence produced in the excitation process is quickly destroyed. In this case the population $p(t)$ decays like the superposition of exponentials weighted with the probability density $N(\gamma)$:

$$p(t) = \int N(\gamma) \exp(-2\gamma t) d\gamma \,. \tag{4.1}$$

We see from Eq. (3.8) that $p(t)$ is formally equivalent to the characteristic function $Q(\beta)$ of $N(\gamma)$ taken at the argument $\beta = -2it$. Identifying thus $Q(-2it)$ with $p(t)$, β has the meaning of an imaginary time constant. It means $p(t)$ relates in the limits of short and long times to the asymptotic expansions of $q(\beta)$ for small and large arguments β, respectively. With this in mind we can define now limiting cases.

1. Large l-level width and short-time limit

This limit is specified by the conditions

$$\rho_0 \overline{\gamma'} \gg 1 \text{ and } t < \frac{\overline{\gamma'}}{V^2} \,, \tag{4.2}$$

with the mean amount deviations of the l-level width from the s-level width

$$\overline{\gamma'} \equiv \langle |\gamma_l - \gamma_0| \rangle \,. \tag{4.3}$$

Eqs. (3.29)–(3.33) show that β enters $q(\beta)$ via the functions $F(\alpha_1)$ and $F(\alpha_2)$. Since their arguments increase linearly with β, due to Eq. (3.30), we have to consider here the expansion of $F(\alpha)$ for small arguments α (Appendix B):

$$F(\alpha) = \frac{5}{3} + \frac{i}{2}\alpha \ln\left(\frac{i\alpha}{2}\right) + \left(\frac{C}{2} - \frac{9}{20}\right) i\alpha + O\left(\alpha^2\right) \,. \tag{4.4}$$

Inserting this expansion into (3.29), we obtain for $q > 0$

$$q(\beta) = i\beta\gamma_{\rm m} + \frac{\pi\rho_0 V^4}{20\Delta\gamma_0} |\ln(q)| \beta^2 + O\left(\rho_0 \overline{\gamma'} \alpha_{1,2}^3\right) \tag{4.5}$$

with

$$\gamma_{\rm m} = \frac{\pi}{3}\rho_0 V^2 \frac{|q| - 1}{|q - 1|} \,, \tag{4.6}$$

and

$$q = \frac{\gamma_2'}{\gamma_1'} = \frac{\gamma_2 - \gamma_0}{\gamma_1 - \gamma_0}\,, \tag{4.7}$$

where we introduced $\gamma_{1,2} = \gamma_0 + \gamma_{1,2}'$. For $q < 0$ follows from (3.29)

$$q(\beta) = i\beta\gamma_{\mathrm{m}} + \left(0.09 - \frac{C}{10}\right)\frac{\pi\rho_0 V^4}{\Delta\gamma_0}\beta^2 - \frac{\pi\rho_0 V^4}{10\Delta\gamma_0}\beta^2 \ln(q_0|\beta|) + O\left(\rho_0\overline{\gamma'}\alpha_{1,2}^3\right) \tag{4.8}$$

with

$$q_0 = \frac{V^2}{4\sqrt{|\gamma_1'\gamma_2'|}}\,. \tag{4.9}$$

To get an estimate of the third order term within the Eqs. (4.5) and (4.8) we take the relative boundaries γ_1' and γ_2' and the extension of the l-level width distribution to be equal as $\overline{\gamma'}$.

We further approximate in (4.8) the function $\beta\ln(q_0|\beta|)$ by the double parabola

$$p(\beta) = \mathrm{sign}(\beta)\left[eq_0\left(|\beta| - \frac{1}{eq_0}\right)^2 - \frac{1}{eq_0}\right]\,, \tag{4.10}$$

with Euler's number $e = 2.718\ldots$, which agrees in its extrema and in the root at $\beta = 0$ with the original function. Thus we obtain for $q(\beta)$ the approximation

$$q(\beta) = i\beta\gamma_{\mathrm{m}} + \frac{\Delta_{\mathrm{G}}^2}{4\pi}\beta^2 + O\left(\rho_0 V^6/\overline{\gamma'}^2\beta^3\right) \tag{4.11}$$

with

$$\Delta_{\mathrm{G}} = \pi V^2\sqrt{\frac{\rho_0}{\Delta\gamma_0}}\begin{cases}\sqrt{|\ln(q)|/5} & \text{if } q > 0\\ \sqrt{1.16 - 0.4C} & \text{if } q < 0\end{cases}\,, \tag{4.12}$$

and Euler's constant $C = 0.57721\ldots$. Neglecting third and higher order term in β in Eq. (4.11) and in Eq. (3.14) for $Q(\beta)$, we get from Eq. (3.9) a Gaussian integral for $N(\gamma)$, yielding the Gaussian width distribution [5]

$$N(\gamma) = \Delta_{\mathrm{G}}^{-1}\exp\left(-\pi\frac{(\gamma - \gamma_{\mathrm{mp}})^2}{\Delta_{\mathrm{G}}^2}\right) \tag{4.13}$$

with

$$\gamma_{\mathrm{mp}} = \gamma_0 + \gamma_{\mathrm{m}}\,. \tag{4.14}$$

This result is justified for the small time limit. It holds particularly well for the main portion of the decay function $p(t)$ and the width distribution $N(\gamma)$ as long as the third order term is small within the range of β where $N(\gamma)$

differs essentially from zero. Comparing the order of magnitudes $\rho_0 V^4/\overline{\gamma'}\beta^2$ and $(\rho_0 V^4/\overline{\gamma'}\beta^2)^{3/2}/\sqrt{\rho_0\overline{\gamma'}}$ of the second and third order terms, one sees that this condition is met if the above condition (4.2) for the level width holds true. The short-time approximation might fail however for times, where $p(t)$ is nearly zero. For the width distribution $N(\gamma)$ this corresponds to a small width region above zero where γ is small compared to the most probable width $\gamma_{\rm mp}$.

2. Small *l*-level width limit and long-time limit

This limit prevails for

$$\rho_0\overline{\gamma'} \ll 1 \;\text{ and }\; t > \frac{\overline{\gamma'}}{V^2}\,. \tag{4.15}$$

Considering now in Eqs. (3.29)–(3.33) for $F(\alpha)$ the asymptotic expansion for large arguments (Appendix B)

$$F(\alpha) = \frac{5}{3}\sqrt{\frac{2}{i\pi\alpha}} + O\left(|\alpha|^{-3/2}\right)\,, \tag{4.16}$$

we get for $q > 0$, which means that $\gamma_0 < \gamma_1, \gamma_2$ or $\gamma_0 > \gamma_1, \gamma_2$

$$q(\beta) = r_-[\mathrm{sign}(\gamma_2') + i\,\mathrm{sign}(\beta)]\sqrt{|\beta|} + O\left(\frac{\rho_0}{V}\overline{\gamma'}^{3/2}|\beta|^{-1/2}\right)\,, \tag{4.17}$$

and for $q < 0$ which implies $\gamma_1 < \gamma_0 < \gamma_2$

$$q(\beta) = [r_+ + ir_-\mathrm{sign}(\beta)]\sqrt{|\beta|} + O\left(\frac{\rho_0}{V}\overline{\gamma'}^{3/2}|\beta|^{-1/2}\right) \tag{4.18}$$

with

$$r_\pm = \frac{\sqrt{2\pi}\rho_0 V}{3\Delta\gamma_0}\left(|\gamma_2'|^{3/2} \pm |\gamma_1'|^{3/2}\right)\,. \tag{4.19}$$

We may perform now the transform (3.9) using Eq. (3.14) for $Q(\beta)$ and, depending on the sign of q, the expressions (4.17) or (4.18) for $q(\beta)$. Neglecting terms of the order $|\beta|^{-1/2}$, we obtain a Gaussian integral. By substituting the new variable $\sqrt{|\beta|}$, applying subsequently Eq. (7.4.2) of Ref. [9] we get [5] for $q > 0$

$$N(\gamma) = \{1 + \mathrm{sign}[(\gamma-\gamma_0)\gamma_2']\}\frac{|r_-|}{2\sqrt{2\pi}|\gamma-\gamma_0|^{3/2}}\exp\left(-\frac{r_-^2}{2|\gamma-\gamma_0|}\right), \tag{4.20}$$

with the most probable value

$$\gamma_{\rm mp} = \gamma_0 + \frac{r_-^2}{3}\mathrm{sign}(\gamma_2')\,, \tag{4.21}$$

and for $q < 0$ follows

$$N(\gamma) = \frac{1}{2\sqrt{\pi}}\mathrm{Re}\left\{-\frac{r_+ + ir_-}{[-i(\gamma-\gamma_0)]^{3/2}} w\left(i\frac{r_+ + ir_-}{2[-i(\gamma-\gamma_0)]^{1/2}}\right)\right\} \tag{4.22}$$

with [(7.1.4) in Ref. [9]]

$$w(z) = \exp\left(-z^2\right)[1 - \mathrm{erf}(-iz)]\,, \tag{4.23}$$

and erf for the Gaussian error function.

The term of next order which enters $q(\beta)$ differs from the reciprocal of the term of leading order, which is of the order of magnitude $(\rho_0 V\sqrt{\overline{\gamma'}}\sqrt{\beta})^{-1}$, by the factor $(\rho_0\overline{\gamma'})^2$. Condition (4.15) makes sure, that this term is small versus the term of leading order within that range of β-values, where the term of leading order causes intermediate to strong damping of $Q(\beta)$, since it is of the same magnitude or larger than unity. The long-time approximation may fail thus only for small β where $Q(\beta)$ is nearly undamped. This β-range relates via the Fourier back-transform (3.9) predominantly to the large-widths tail of $N(\gamma)$.

5. Results and discussion

The occurrence of the Gaussian distribution for the large level-width limit $\rho_0\langle|\gamma_l - \gamma_0|\rangle \gg 1$ is an outcome of the central-limit theorem. It holds for the decay function particularly in the short-time limit $t < \langle|\gamma_l - \gamma_0|\rangle/V^2$. For long times, deviations from an expotential decay are expected, due to the small widths part of the induced widths distribution. Here we are more interested in the limit of small l-level widths, $\rho_0\langle|\gamma_l - \gamma_0|\rangle \ll 1$, which finds its applications also in the long time limit $t > \langle|\gamma_l - \gamma_0|\rangle/V^2$. In this limit, the width distributions are Lévy-stable distributions. We can distinguish two cases regarding the location of the s-level width with respect to the distribution of the l-level widths. If the s-level width lies outside of that distribution, we get for the widths of the perturbed s-levels the strongly asymmetric distribution (4.20), and Eq. (4.17) holds for function $q(\beta)$, which appears in the exponent of the characteristic function. The resulting distribution can be identified with the Lévy distribution [8] $L_{1/2,\mathrm{sign}(\gamma_2')}(\beta)$. If the s-level width lies within the l-level widths distribution, we get (4.18) for $q(\beta)$, and we can identify $Q(\beta)$ with $L_{1/2,\eta}(\beta)$ with

$$\eta = \frac{1 - |q|^{3/2}}{1 + |q|^{3/2}}\,, \tag{5.1}$$

and (4.7) for q. We see that the first index in the Lévy distribution relates to the nature of the asymmetric time dependence in $p(t)$. Here we find only the value $\epsilon = 1/2$. The second index η depends on the width of the

s-level, γ_0, taken relative to the widths of the l-levels. The figures show the distributions of the induced widths γ rescaled at the most probable width $\gamma_{\rm mp}$ [Eqs. (4.14) and (4.21)]

$$N_0(\Delta\gamma) = \frac{N(\gamma)}{N(\gamma_{\rm mp})} \tag{5.2}$$

as a function of

$$\Delta\gamma = (\gamma - \gamma_{\rm mp})N(\gamma_{\rm mp})\,. \tag{5.3}$$

In Fig. 1, $\gamma_{\rm mp}$ is equal to the s-level width γ_0, and the symmetry parameter q is set equal to -1. This means that γ_0 lies in the center of the linewidth distribution $h(\gamma_l)$. As parameter the dimensionless density

$$\rho = \frac{\pi}{2}\rho_0\gamma_2' \tag{5.4}$$

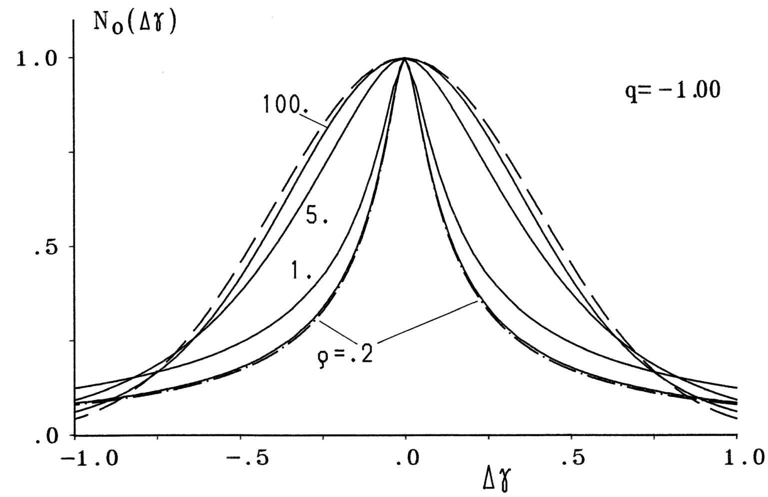

Fig. 1. Width-distributions scaled to the value at the most probable width $\gamma_{\rm mp}$ as function of $\Delta\gamma$ for different values of $\rho = \frac{\pi}{2}\rho_0(\gamma_2 - \gamma_0)$. $\Delta\gamma$ is the deviation of the width of the perturbed s-state, γ, from $\gamma_{\rm mp}$ in units of the distribution width $N(\gamma_{\rm mp})^{-1}$ [Eq. (5.3)]. The full drawn lines show $N_0(\Delta\gamma)$ distributions for different values of ρ, calculated numerically from Eq. (5.2) using Eq. (3.9) for $N(\gamma)$ together with Eq. (3.14) for $Q(\beta)$ and Eq. (4.7) for q. with the box distributions (3.26) and (3.27) for the l-level widths and couplings. The dashed curve shows the Gaussian limit for large ρ. It was obtained from Eq. (4.13). The dashed-dotted line gives the symmetric Lévy distribution for small ρ, and was obtained from Eq. (4.22) using Eq. (4.19) with $|\gamma_1'| = |\gamma_2'|$ for $r\pm$.

is varied between the large l-level width limit, which joins into the Gaussian function (4.13) and the small l-level width limit, which shows for $\rho = 0.2$ and $q = -1$ the sharpened function (4.22). In Fig. 2 the parameter q is taken positive, and the s-level width γ_0 lies to the left of the l-level width distribution, and the dashed and dash dotted curves show the rescaled limiting distributions for the induced widths $\gamma - \gamma_{mp}$ in cases of large l-level widths and small l-level widths bigger than the s-level width. In case of large l-level widths the Gaussian distribution (4.13) results, and for small l-level widths the Lévy distributions (4.20) with $\text{sign}(\gamma_2') = 1$ emerge for the induced width $\gamma - \gamma_{mp}$. It can be seen, that the distribution function changes from a Gaussian distribution in the limit of large l-level widths to a very asymmetric distribution for the limit of small l-level widths.

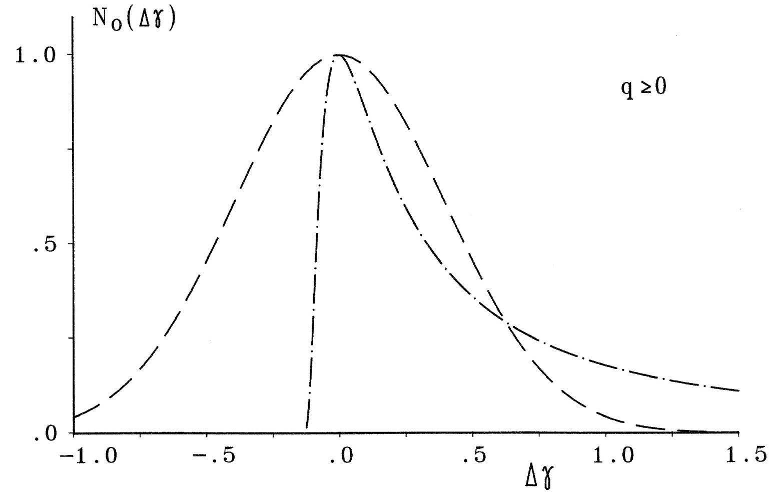

Fig. 2. Limiting width distributions for large and small ρ. For scaling see Fig. 1. The dashed curve shows the distribution for a dense dark manifold. It is the same as in Fig. 1. The dashed-dotted curve was obtained from Eq. (4.20) for $\gamma_2' > 0$ with the lower sign (4.19) for r_-. It shows the limiting asymmetric Lévy distribution for the case that the dark-state widths are bigger than the width of the bright state, γ_0.

While the decay pattern of the Gaussian limit can be well characterized by an exponential with a decay time given by the inverse of the width Γ_u of (2.22), depending on the $f(E)$ distribution, strong deviations can result for the long tail distribution in the limit of small l-level widths. The decay depends, however, on the nature of the excitation pulse and the destruction of the coherence. As long as the coherence within the distribution is preserved and the excitation pulse covers essentially the full line, an exponential decay will result, given again by the inverse of the width Γ_u. However, if the distributions change in time, they will destroy the coherence, and the long time limit is characterized by the decay function (4.1) which is given then by $Q(\beta)$ with $\beta = -2it$ and Eq. (4.17) for $q(\beta)$ with $\mathrm{sign}(\gamma_2') = \pm 1$. Here the upper or the lower sign holds, respectively, if all l-level widths are larger or smaller than the s-level width. In the latter case the s-state width is diminished, and $p(t)$ diverges due to a missing cut-off of $N(\gamma)$ for negative widths γ. Confining to the former mentioned case, the s-state 'borrows' widths from the l-levels. Substituting in Eq. (4.17) $[1 + i\,\mathrm{sign}(\beta)]\sqrt{|\beta|} = \sqrt{2i\beta} = 2\sqrt{t}$, we obtain a square-root dependence of $p(t)$, which stems from the long-time small valued γ distributions. It consists of separately decaying states with survival probabilities

$$p(t) = \langle |\langle s|s(t)\rangle|^2 \rangle = \exp\left(-2\gamma_0 t - 2r_- \sqrt{t}\right) \tag{5.5}$$

with r_- given in Eq. (4.19).

6. Summary

We studied the random matrix model of a bright state coupled to a manifold of dark states under two conditions with regard to the energy distribution function of the dark states: the nearly degenerate limit and the unbounded energy limit. Both limits provide Lorentzian line shape functions under very general conditions for the coupling distributions and the width distributions. We analyzed in detail the distribution of the level widths induced via the couplings from the dark states into the bright state. For the quasidegenerate limit we obtained the Gaussian distribution provided a sufficiently large number of dark levels contributed to the broadening of the bright state. However, for the case where a single level would contribute with Gauss distributed couplings, we recovered the Porter–Thomas distribution function for the induced widths. For the case of the unbounded energy distribution we obtained as limiting cases either Gaussian distributions or Lévy distributions depending on the magnitude of the parameter $\rho_0\langle|\gamma_l - \gamma_0|\rangle$. For the large level-width and small-time limit we found a Gaussian distribution but for the small-level width and large-time limit we found Lévy distributions with Lévy indices depending upon the location of the width of the bright state relative to the location of the dark-state width distribution. We consider this latter result as most remarkable, since it relates different Lévy distribution functions to the width distributions of the dark states. Interestingly, only two parameters, r_+ and r_- [Eq. (4.19)] are needed to specify the Lévy function, even though four were needed to specify the dark level distributions, namely the mean density of dark states ρ_0, the locations $\gamma_{1,2}$ of the boundaries of the dark level width distribution relative to the width of the bright state, and the extension $2V$ of the symmetric coupling distribution. The exponent in the Lévy function characterizing the long-time dependence of the survival probability comes out always as $\eta = 1/2$.

Appendix A

Evaluation of the integral (3.28)

After performing in Eq. (3.28) the transform onto the new integration variables $\gamma' = \gamma_l - \gamma_0$ and $\tau = v^2/\gamma'$, the old variable v writes $\mathrm{sign}(\gamma')\sqrt{\gamma'}\sqrt{\tau}$, where we accounted for the positive sign of v with the proper prefactor. We hence have to transform the differential dv in Eq. (3.28) as

$$dv = \mathrm{sign}(\gamma')\frac{\sqrt{\gamma'}}{2\sqrt{\tau}}d\tau\,, \tag{A.1}$$

and substitute there $\beta\tau/2$ for β_l [Eq. (3.24)]. Thus we get

$$q(\beta) = \frac{i\pi\rho_0}{2V\Delta\gamma_0}\int_{\gamma_1'}^{\gamma_2'} d\gamma' \int_0^{\tau_0(\gamma')} d\tau\beta\gamma'^{3/2}\sqrt{\tau}\Phi\left(\frac{\beta\tau}{2}\right)\,, \tag{A.2}$$

where the upper integration boundary of the second integral is a function of the first integration variable

$$\tau_0(\gamma') = \frac{V^2}{\gamma'}\,. \tag{A.3}$$

In order to perform in (A.2) the integration over γ' we exchange there the order of integrations. Taking care of the proper integration boundaries in the γ', τ-plane, we distinguish thereby three different combinations of signs for γ_1' and γ_2'. The double integral in Eq. (A.2) then transforms
for $\gamma_1', \gamma_2' > 0$ into

$$\int_0^{V^2/\gamma_2'} d\tau \int_{\gamma_1'}^{\gamma_2'} d\gamma' + \int_{V^2/\gamma_2'}^{V^2/\gamma_1'} d\tau \int_{\gamma_1'}^{V^2/\tau} d\gamma'\,, \tag{A.4}$$

and for $\gamma_1', \gamma_2' < 0$ into

$$\int_0^{V^2/\gamma_1'} d\tau \int_{\gamma_1'}^{\gamma_2'} d\gamma' + \int_{V^2/\gamma_1'}^{V^2/\gamma_2'} d\tau \int_{V^2/\tau}^{\gamma_2'} d\gamma'\,, \tag{A.5}$$

whereas for $\gamma_1'\gamma_2' < 0$ it goes over in

$$\int_0^{V^2/\gamma_1'} d\tau \int_{\gamma_1'}^{0} d\gamma' + \int_{V^2/\gamma_1'}^{-\infty} d\tau \int_{V^2/\tau}^{0} d\gamma' + \int_0^{V^2/\gamma_2'} d\tau \int_0^{\gamma_2'} d\gamma' + \int_{V^2/\gamma_2'}^{\infty} d\tau \int_0^{V^2/\tau} d\gamma' . \quad (A.6)$$

Subsequent to this we can perform in Eq. (A.2) the integration over γ' for these cases. The results subsume in

$$q(\beta) = \frac{i\pi\rho_0}{5V\Delta\gamma_0}\left\{ \int_0^{V^2/\gamma_2'} \beta d\tau \gamma_2'^{5/2}\sqrt{\tau}\Phi\left(\frac{\beta\tau}{2}\right) - \int_0^{V^2/\gamma_1'} \beta d\tau \gamma_1'^{5/2}\sqrt{\tau}\Phi(\beta\tau/2) + \int' \beta d\tau V^5 \tau^{-2}\Phi(\beta\tau/2)\right\} . \quad (A.7)$$

Here we introduced the following abbreviations; for $\gamma_1'\gamma_2' > 0$

$$\int' = \mathrm{sign}(\gamma_1') \int_{V^2/\gamma_2'}^{V^2/\gamma_1'} , \quad (A.8)$$

and for $\gamma_1'\gamma_2' < 0$,

$$\int' = \int_{V^2/\gamma_1'}^{-\infty} + \int_{V^2/\gamma_2'}^{\infty} . \quad (A.9)$$

After substituting into (A.7) the new integration variable $y = \beta\tau/2$, and on proper account of different cases for the phase factors, one recovers Eq. (3.29).

Appendix B

Asymptotic expansions of $F(\alpha)$

1. Small α

Performing a Taylor series expansions of the exponential and the Bessel functions within Eq. (3.25) for the function $\Phi(y)$, we obtain for small arguments

$$\Phi(y) = \left[1 - \frac{i}{2}y + O(y^2)\right] . \quad (B.1)$$

By inserting this result into Eq. (3.32), we get for $F_1(\alpha)$ for small α

$$F_1(\alpha) \equiv \alpha^{-3/2} \int_0^{\alpha} \left[y^{1/2} - \frac{i}{2} y^{3/2} + O\left(y^{5/2}\right) \right] dy = \frac{2}{3} - \frac{i}{5}\alpha + O\left(\alpha^2\right) \,. \quad \text{(B.2)}$$

Using further Eq. (3.25) for $\Phi(y)$, by substitution of the new integration variable $z = \mathrm{sign}(\alpha) y$, we obtain from Eq. (3.33)

$$F_2(\alpha) = |\alpha| \int_{|\alpha|}^{\infty} e^{-i\mathrm{sign}(\alpha)z} z^{-2} J_0(z) dz + i\alpha \int_{|\alpha|}^{\infty} e^{-i\mathrm{sign}(\alpha)z} z^{-2} J_1(z) dz \,. \quad \text{(B.3)}$$

Invoking here for the integrals the asymptotic expansions for small arguments, given by Eq. (9) of Section 4.2 in Ref. [10] with $\mu = -2$, $\nu = 0$ and $\nu = 1$ and by the complex conjugate of this equation, we obtain after a little algebra

$$F_2(\alpha) = 1 + \frac{i}{2}\alpha \ln \frac{i\alpha}{2} + \left(\frac{C}{2} - \frac{1}{4} \right) i\alpha \,. \quad \text{(B.4)}$$

By substituting this result together with (B.2) for $F_1(\alpha)$ into Eq. (3.31), we arrive at Eq. (4.4).

2. Large α

We first rewrite Eq. (3.32) for $F_1(\alpha)$ by performing there integration by parts to get

$$F_1(\alpha) = \Phi(\alpha) - 2\alpha^{-3/2} \int_0^{\alpha} y^{1/2} \frac{d[y\Phi(y)]}{dy} dy \,, \quad \text{(B.5)}$$

and, by using the relations (9.1.27) of Ref. [9] for the derivatives of Bessel functions, we find

$$F_1(\alpha) = 2\Phi(\alpha) - 2\alpha^{-3/2} \int_0^{\alpha} y^{1/2} e^{-iy} J_0(y) dy \,. \quad \text{(B.6)}$$

We may write this as

$$\begin{aligned} F_1(\alpha) = \quad & 2\Phi(\alpha) - 2\alpha^{-3/2} e^{-i\alpha} \Bigg[\int_0^{\alpha} y^{1/2} \cos(\alpha - y) J_0(y) dy \\ & + i \int_0^{\alpha} y^{1/2} \sin(\alpha - y) J_0(y) dy \Bigg] \,. \end{aligned} \quad \text{(B.7)}$$

Expanding the integrals in terms of Bessel functions, as in Eqs. (6.716.1) and (6.716.2) of Ref. [11] with $\lambda = 1/2$ and $\nu = 0$, we get

$$F_1 = 2e^{-i\alpha}\left[\frac{1}{3}J_0(\alpha) + iJ_1(\alpha) - 2\frac{\Gamma(3/2)}{\Gamma(-1/2)}\sum_{n=1}^{\infty} i^n \frac{\Gamma(n-3/2)}{\Gamma(n+5/2)} nJ_n(\alpha)\right] . \quad \text{(B.8)}$$

Using further Eq. (9.2.1) of Ref. [9] together with symmetry of trigonometric and Bessel functions, we obtain expansions for large real arguments of the Bessel function $J_n(\alpha)$. For even n we have

$$J_n(\alpha) = i^n \sqrt{\frac{2}{\pi|\alpha|}}\left[\cos\left(|\alpha| - \frac{\pi}{4}\right) + O\left(|\alpha|^{-1}\right)\right] , \quad \text{(B.9)}$$

and for odd n

$$J_n(\alpha) = i^{n-1}\text{sign}(\alpha)\sqrt{\frac{2}{\pi|\alpha|}}\left[\sin\left(|\alpha| - \frac{\pi}{4}\right) + O\left(|\alpha|^{-1}\right)\right] . \quad \text{(B.10)}$$

By inserting these results into Eq. (B.8), we obtain for large α

$$F_1 = \sqrt{\frac{2}{\pi|\alpha|}} e^{-i\alpha}\left[\left(\frac{1}{3} - \Sigma_+\right)\cos\left(|\alpha| - \frac{\pi}{4}\right) + i\,\text{sign}(\alpha)(1 - \Sigma_-)\sin\left(|\alpha| - \frac{\pi}{4}\right)\right] + O\left(\alpha^{-3/2}\right) , \quad \text{(B.11)}$$

with

$$\Sigma_\pm = \frac{\Gamma(3/2)}{\Gamma(-1/2)}\sum_{m=0}^{\infty}\frac{\Gamma(m+2)\Gamma(m-1/2)}{\Gamma(m+7/2)m!}[1 \mp (-1)^m] . \quad \text{(B.12)}$$

We may sum up this series in terms of Hypergeometric Functions [Eqs. (15.1.1), (15.1.20) and (15.1.21) in Ref. [9]],

$$\Sigma_\pm = \frac{\Gamma(3/2)}{\Gamma(7/2)}\left[F\left(2, -\frac{1}{2}; \frac{7}{2}; 1\right) \mp F\left(2, -\frac{1}{2}; \frac{7}{2}; -1\right)\right] = 1/6 \mp 1/3 , \quad \text{(B.13)}$$

and with this result we get from (B.11) after a little algebra

$$F_1 = \sqrt{\frac{2}{i\pi\alpha}} + O\left(\alpha^{-3/2}\right) . \quad \text{(B.14)}$$

Using further in Eq. (3.25) the Eqs. (B.9) and (B.10) with $n = 0$ and $n = 1$, we obtain for $\Phi(y)$ for large real arguments y

$$\Phi(y) = \sqrt{\frac{2}{\pi|y|}} e^{-i\mathrm{sign}(y)\frac{\pi}{4}} , \tag{B.15}$$

and by inserting this expansion for $\Phi(y)$ into (3.33) we obtain for large real arguments α

$$F_2(\alpha) = \alpha\sqrt{\frac{2}{\pi}} e^{-i\mathrm{sign}(\alpha)\frac{\pi}{4}} \int_{\alpha}^{(\mathrm{sign}(\alpha))\infty} \Big[|y|^{-5/2} + O\left(|y|^{-7/2}\right)\Big] dy = \frac{2}{3}\sqrt{\frac{2}{i\pi\alpha}} + O\left(\alpha^{-3/2}\right) . \tag{B.16}$$

By substituting this result together with Eq. (B.14) for $F_1(\alpha)$ into Eq. (3.31), we finally arrive at Eq. (4.16) for $F(\alpha)$.

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