Infinite-order non-Born-Oppenheimer perturbation theory for systems with intersecting potentials

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We analyze models for two intersecting electronic states coupled by one nuclear coordinate. The corresponding model-Hamiltonians depend on a perturbation parameter α. Its variation allows us to switch on the nonadiabatic coupling continuously. We derive analytical expressions for the eigenstates and energies as function of α in the diabatic representation. We rederive the expression for the energy eigenvalues by complete resummation of the Brillouin-Wigner perturbation series in the Born-Oppenheimer basis. We find that the divergences of the nonadiabatic coupling cancel strictly order by order. The admixture of high energy components is shown explicitly.

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I. INTRODUCTION

The intersection of potential energy surfaces and, linked with it, the breakdown of the Born-Oppenheimer (BO) approximation[1] has attracted considerable interest as, after a prediction by Teller [7,8], so-called ''conical intersections'' have turned out to play a key role in the path of photochemical reactions [9]. These conical intersections have been systematically classified [10] as codimension two-crossings. Also the conceptually simpler codimension one-crossings appear in molecular physics, e.g., in the $E\times\beta$ Jahn-Teller effect [11]. This effectively one-dimensional crossing is representable as a limit of avoided intersections. In this limit, the nonadiabatic (NA) coupling matrix elements diverge seriously, so that they are not even representable in a distributional sense. If we write the Hamiltonian as

$$H=H^{\mathrm{BO}}+H^{\mathrm{NA}}, \tag{1.1}$$

one can distinguish the nondiagonal nonadiabatic elements H^{ND} from the diagonal (Born-Huang) one H^{D} so that

$$H^{\mathrm{NA}}=H^{D}+H^{\mathrm{ND}}. \tag{1.2}$$

Wagner [12] and Špirko *et al.* [13,14] independently studied this problem treating the NA-coupling perturbationally. If we call the perturbation parameter α, Wagner studied two cases:

$$H_{\alpha}=H^{\mathrm{BO}}+\alpha H^{D}+\alpha H^{\mathrm{ND}} \tag{1.3}$$

and

$$H_{\alpha}=H^{\mathrm{BO}}+H^{D}+\alpha H^{\mathrm{ND}}, \tag{1.4}$$

which both reduce to Eq. (1.1) in the limit $\alpha=1$. In zeroth order Eq. (1.3) corresponds to the BO approximation, while Eq. (1.4) corresponds to the Born-Huang adiabatic approximation. Wagner came to the conclusion that neither the first nor the second expression can be taken as a legitimate zero-order Hamiltonian to establish a perturbation expansion. Similar objections are widespread in the literature [15].

On the other hand Špirko *et al.*, start from Eq. (1.4) and calculate numerically the Rayleigh-Schrödinger series for near-avoided intersections. Although sometimes divergent, this series can be Padé-summed to give the correct result. As has been noted already by Teller [7,8], the Born-Huang term, which is most divergent at an intersection, gives a contribution of the same order of magnitude as the square of the nondiagonal terms. It therefore appears natural to use an α-dependent Hamiltonian of the form

$$H_{\alpha}=H^{\mathrm{BO}}+\alpha^{2}H^{D}+\alpha H^{\mathrm{ND}}. \tag{1.5}$$

For the case of a two-state system as studied in [12,13] we then show that for an intersection, the most serious divergences in the energy series cancel within each order. Further, for each value of α, we are then able to construct an equivalent diabatic Hamiltonian whose eigenenergies are easily found. Under the further restriction that the Hamiltonian possesses a Fulton-Gouterman mirror symmetry [16], we construct the whole perturbation series explicitly and show that resummation gives the energies known already from the diabatic representation.

II. THE TWO-STATE MODEL FOR AN INTERSECTION

We want to start with a Hamiltonian, consisting of two electronic states and one vibrational degree of freedom x, with quite general diagonal $g(x)$ and nondiagonal $f(x)$ interaction potentials,

$$H^{\mathrm{DIA}}=\frac{1}{2}\left\{\left(-\frac{d^{2}}{dx^{2}}+2U(x)\right)\sigma_{0}+f(x)\sigma_{1}-g(x)\sigma_{3}\right\}. \tag{2.1}$$

σ_0 is the 2×2 unit matrix and the σ_i with $i=1,2,3$ are the usual Pauli matrices. We define further the projectors on the eigenstates $|\uparrow/\downarrow\rangle$ of σ_3, $\sigma_{\uparrow/\downarrow}=\frac{1}{2}(1\pm\sigma_3)$. The variable ζ may take the two values $\uparrow$ and $\downarrow$. If $\zeta=\uparrow/\downarrow$, then $\bar{\zeta}=\downarrow/\uparrow$, i.e., the slash symbolizes interchange of the values.

[1]The term BO-approximation [1–5] is used, often without distinction, to designate a couple of different although related methods. We will use the term BO-approximation and other nomenclature as defined in [4] (for a critical review of terminology, see [6]).

This Hamiltonian has been used by Špirko and Cižek [13]. It is given in a diabatic representation. In the following we specify the terminus ''intersection.''

If for some value x_0, the function $\sqrt{f^2(x)+g^2(x)}$ has a minimum, we speak of an avoided intersection. Further if $\sqrt{f^2(x_0)+g^2(x_0)}=0$, which clearly includes both $f(x_0)=0$ and $g(x_0)=0$, we speak of a true intersection.

The meaning of this definition will become clearer if we switch to the Born-Oppenheimer adiabatic representation by means of the unitary operator

$$S=\exp[iP(x)\sigma_2], \tag{2.2}$$

with

$$P(x)=\frac{1}{2}\arctan\frac{f(x)}{g(x)}. \tag{2.3}$$

The transformed Hamiltonian $\tilde{H}$, now in the adiabatic representation is

$$\tilde{H}=S^+H^{\mathrm{DIA}}S=H^{\mathrm{BO}}+H^{\mathrm{NA}}. \tag{2.4}$$

It splits into two parts, namely, the Born-Oppenheimer part

$$\begin{aligned}H^{\mathrm{BO}}&=\frac{1}{2}\left\{\left(-\frac{d^2}{dx^2}+2U(x)\right)\sigma_0-\sqrt{f^2(x)+g^2(x)}\sigma_3\right\}\\&=H_{a\uparrow}\sigma_\uparrow+H_{b\downarrow}\sigma_\downarrow,\end{aligned} \tag{2.5}$$

and the nonadiabatic part,

$$H^{\mathrm{NA}}=-\frac{1}{2}S^+\left[\frac{d^2}{dx^2},S\right]=\frac{1}{2}(\{p,P'(x)\sigma_2\}+[P'(x)]^2\sigma_0). \tag{2.6}$$

In the adiabatic representation the potential is now diagonal, while nondiagonal contributions are found in the kinetic energy. Now we see that the distance of the potential energy curves of the adiabatic states will be minimal at x_0 if we have an avoided intersection, or it will be zero for a true intersection.

We fix the origin of our coordinate system so that it coincides with the locus of the intersection, $x_0=0$. Applying a global gauge transformation, $\exp(iw\sigma_2)$, with an appropriately chosen constant w, we may always achieve $f(0)=0$. On the other hand, from the definition of an avoided intersection it then follows that $f(0)f'(0)+g(0)g'(0)=g(0)g'(0)=0$, so that $g'(0)=0$, too.

In the following we analyze the various contributions to the nonadiabatic coupling Hamiltonian (2.6): The anticommutator on the right-hand-side (rhs) of Eq. (2.6) represents a momentum-dependent coupling of the electronic states, while the second term is known as Born-Huang perturbation term. If we reduce the value $\tilde{\gamma}:=g(0)$, the nonadiabatic term $P'(x)$ will be more and more spiked at $x=0$, the shape of the spike will be locally Lorentzian with a width proportional to $\tilde{\gamma}$ [Eq. (4.10)]. Depending on which functions this operator acts, we can sometimes interpret it in the limit $\tilde{\gamma}\to 0$ as Dirac's delta-function. The intricacies of this limiting process will be discussed in Appendix D. The Born-Huang term will then be seriously divergent as it is proportional to $[P'(x)]^2$ and so diverges like the square of a delta function. These divergencies represent the interesting feature appearing at intersections that we want to study. On the other hand, these divergencies depend only on the vanishing of $g(0)$, we therefore will restrict our calculations to the case that $g(x)$ is a constant $g(x)=\tilde{\gamma}$.

As we pursue a perturbational treatment, we have to introduce a perturbation parameter α into the Hamiltonian. In this case we are no longer considering a single Hamiltonian, but a whole class of them. For perturbation theory (PT), these Hamiltonians have to be well defined for a whole range of values of α. Due to the strong divergence of the Born-Huang term in the limit $\tilde{\gamma}\to 0$, the proper introduction of α will be of crucial importance. Teller [8] noted already that the nondiagonal terms first contribute to the energy in second order, but then their contribution is about that of the Born-Huang term. So it seems advantageous to replace $P(x)$ by $\alpha P(x)$. Indeed with this choice we will be able to show that the worst divergent terms cancel exactly order by order. We now write the nonadiabatic part as

$$\begin{aligned}H^{\mathrm{NA}}_\alpha&=-\frac{1}{2}S^+_\alpha\left[\frac{d^2}{dx^2},S_\alpha\right]\\&=\frac{1}{2}[\{p,\alpha P'(x)\sigma_2\}+\{\alpha P'(x)\}^2\sigma_0],\end{aligned} \tag{2.7}$$

with

$$S_\alpha:=\exp[i\alpha P(x)\sigma_2]. \tag{2.8}$$

For $\alpha=1$ this clearly reduces to Eq. (2.6), while for $\alpha=0$ the nonadiabatic coupling vanishes at all, so that the BO treatment becomes exact.

Before proceeding, we note that for $\alpha=1$, $g(x)$ vanishes identically and Eq. (2.1) is diagonalized (and still diabatic) with $\tilde{S}=\exp(i\sigma_2\pi/4)$ because this transformation changes σ_1 into σ_3 and σ_3 into $-\sigma_1$.

As an example consider $U(x)=x^2/2+1$, $f(x)=2\sqrt{2}x$, and $g(x)=0$. Again for $\alpha=1$, the above mentioned diagonal diabatic potentials have the shape of parabola with the vertices shifted to $x=\pm\sqrt{2}$. The adiabatic potentials, which by definition do not depend on α, are similar, but with a different connection of the branches at $x=0$, so that in effect we get one W-shaped and one V-shaped potential, $V_{a\uparrow/b\downarrow}=x^2/2+1\mp|\sqrt{2}x|$ (Fig. 1).

III. EXACT SOLUTION IN THE DIABATIC BASIS

Applying the inverse of transformation (2.4) and using the generalized operators (2.7),(2.8), we can introduce a generalized diabatic representation

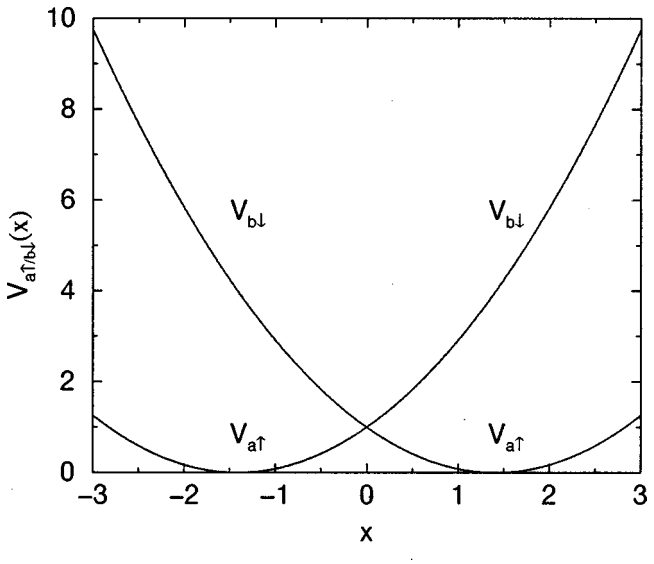

FIG. 1. The adiabatic potentials $V_{a\uparrow/b\downarrow}(x)$.

$$H_\alpha^{\mathrm{DIA}} = S_\alpha \tilde{H}_\alpha S_\alpha^+ = \frac{1}{2}\left[\left(-\frac{d^2}{dx^2}+2U(x)\right)\sigma_0 - \sqrt{f^2(x)+g^2(x)} \times[-\sin\{2\alpha P(x)\}\sigma_1+\cos\{2\alpha P(x)\}\sigma_3]\right]. \tag{3.1}$$

For $g(x)=0$, as we will assume in the rest of this chapter, we get

$$H_\alpha^{\mathrm{DIA}} = \frac{1}{2}\left(-\frac{d^2}{dx^2}+2U(x)\right)\sigma_0 + \frac{1}{2}\left[\sin\left(\alpha\frac{\pi}{2}\right)f(x)\sigma_1 - \cos\left(\alpha\frac{\pi}{2}\right)|f(x)|\sigma_3\right]. \tag{3.2}$$

If $\alpha=0$, we get back the BO Hamiltonian (2.5) while for $\alpha=1$, we get the original diabatic Hamiltonian (2.1). We note that our problem is periodic in α with period 4. The spectrum has a period 2 and depends only on $|\alpha|$.

In the following we evaluate the eigenstates $\phi(x)=(\phi_\uparrow(x),\phi_\downarrow(x))^T$ and eigenenergies $\tilde{E}$ of Eq. (3.2) for any value of α. As the diabatic and adiabatic representations are related via an unitary transformation, we solve in the same breath also the adiabatic problem (2.4).

Unlike the nonadiabatic Hamiltonian (2.4), the diabatic Hamiltonian contains only potential terms that are finite, especially at $x=0$. Therefore, the wave functions and their logarithmic derivatives must be continuous there. Though, the strategy we will apply is to solve the equation on the left- and right-half-axis separately and finally patch the two solutions at $x=0$. Although it is straightforward to do so for general $U(x)$ and $f(x)$, we will only derive results for the case where the Hamiltonian possesses so-called Fulton-Gouterman symmetry [16], which means here that $f(-x)=-f(x)$ and $U(-x)=U(x)$.

We note that

$$S_\alpha := \exp\left(i\alpha\frac{\pi}{4}\mathrm{sgn}(x)\sigma_2\right) = \begin{cases} T^+, & x<0 \\ T, & x>0 \end{cases} \tag{3.3}$$

with

$$T = \cos\left(\alpha\frac{\pi}{4}\right)\sigma_0 + i\sin\left(\alpha\frac{\pi}{4}\right)\sigma_2, \tag{3.4}$$

which does not depend on x. For $x\neq 0$ the Hamiltonian (2.4) will reduce to the BO Hamiltonian (2.5). On the positive half-line we introduce eigenstates of the latter as

$$H_{z\zeta}\psi_z^\zeta = \tilde{E}\psi_z^\zeta, \tag{3.5}$$

which should fulfill the boundary conditions

$$\psi_z^\zeta(0)=1 \quad \text{and} \quad \psi_z^\zeta(+\infty)=0. \tag{3.6}$$

Due to symmetry, we have the solutions $\psi_z^\zeta(-x)$ on the negative half-line. For the diabatic wave function, we get

$$\phi(x) = \begin{cases} T^+(v_\uparrow\psi_a^\uparrow(-x), v_\downarrow\psi_b^\downarrow(-x))^T, & x<0 \\ T(w_\uparrow\psi_a^\uparrow(x), w_\downarrow\psi_b^\downarrow(x))^T, & x>0, \end{cases} \tag{3.7}$$

where we still have to determine the constants w_ζ and v_ζ. Symmetry requires $\pm w_\uparrow = v_\uparrow$ and $\mp w_\downarrow = v_\downarrow$. The continuity condition at $x=0$ reads

$$T^+(\pm w_\uparrow, \mp w_\downarrow)^T = T(w_\uparrow, w_\downarrow)^T \tag{3.8}$$

or

$$\sigma_3 T(w_\uparrow, w_\downarrow)^T = \pm T(w_\uparrow, w_\downarrow)^T. \tag{3.9}$$

So, up to an overall normalization constant, we either have $w_\uparrow=\cos(\alpha\pi/4)$ and $w_\downarrow=\sin(\alpha\pi/4)$, or $w_\uparrow=-\sin(\alpha\pi/4)$ and $w_\downarrow=\cos(\alpha\pi/4)$. Defining

$$\lambda_{z\zeta} := \frac{d\psi_z^\zeta(0)}{dx} \Big/ \psi_z^\zeta(0) \tag{3.10}$$

as the logarithmic derivative of $\psi_z^\zeta(x)$ at $x=0$, we get the logarithmic derivative of $\psi_z^\zeta(-x)$ as $-\lambda_{z\zeta}$. Since the logarithmic derivative must be continuous too, it follows that

$$\sigma_3 T(w_\uparrow\lambda_{a\uparrow}, w_\downarrow\lambda_{b\downarrow})^T = \mp T(w_\uparrow\lambda_{a\uparrow}, w_\downarrow\lambda_{b\downarrow})^T \tag{3.11}$$

holds, and from this, we infer the result

$$-\frac{\lambda_{a\uparrow}}{\lambda_{b\downarrow}} = \tan^2\left(\alpha\frac{\pi}{4}\right) \tag{3.12}$$

for the plus sign in Eq. (3.9), or

$$-\frac{\lambda_{a\uparrow}}{\lambda_{b\downarrow}} = \cot^2\left(\alpha\frac{\pi}{4}\right) \tag{3.13}$$

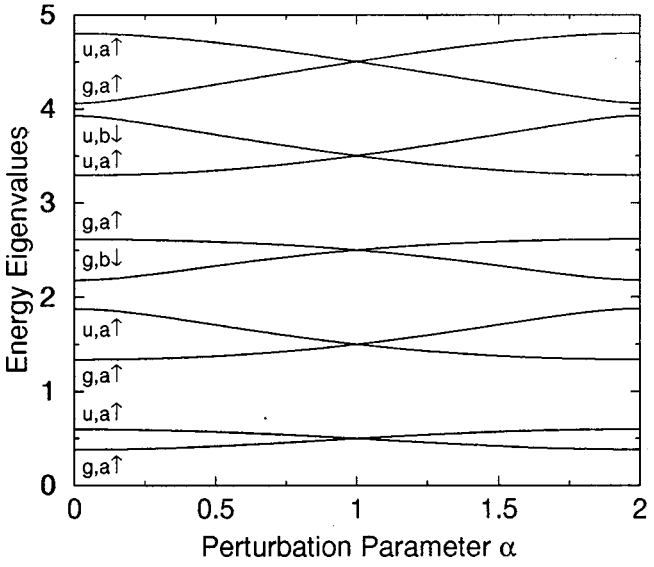

FIG. 2. The spectrum for different values of α.

for the minus sign. Indeed, as the logarithmic derivative is a function of the energy, these last two expressions are implicit equations for the possible energy eigenvalues $\tilde{E}$ in dependence of the parameter α.

We note that the Hamiltonians (3.1) for different values of α are identical for $x\neq 0$. They are therefore merely different self-adjoint extensions whose domains contain functions fulfilling different boundary conditions at $x=0$. It may be viewed as another type of point interaction [17], which are of interest also in other branches of physics, e.g., relativistic quantum mechanics.

For $U(x)$ and $f(x)$ from the end of the second section, we can express the functions ψ_z^ζ as parabolic cylinder functions $\psi_a^\uparrow(x)=D_{\tilde{E}_s-1/2}(\sqrt{2}x-2)$ and $\psi_b^\downarrow(x)=D_{\tilde{E}_s-1/2}(\sqrt{2}x+2)$ [18,19]. For $\alpha=1$, the spectrum is that of two degenerate harmonic oscillators. For other values of α, the Eqs. (3.12) and (3.13) can easily be solved numerically (Fig. 2). For $\alpha=0$, the wave functions are either even or odd eigenfunctions of the ''double oscillators'' [19], $H_{a\uparrow}$ or of $H_{b\downarrow}$. We added the corresponding labels in Fig. 2.

IV. PERTURBATIONAL SOLUTION IN THE ADIABATIC BASIS

In this section, we will treat the nonadiabatic coupling using perturbation theory. Assuming Fulton-Gouterman symmetry [$f(-x)=-f(x)$ and $U(-x)=U(x)$], we succeeded in summing analytically the whole series. We think that the main features and peculiarities will survive also in the PT series of the case without symmetry but this is difficult to prove analytically.

To begin, we will cast the Hamiltonian as given by Eqs. (2.5) and (2.8) in an alternative form. In view of Eqs. (3.12) and (3.13) it appears especially advantageous to introduce the notions of supersymmetry (SUSY) [20] (see Appendix C), because in this theory the logarithmic derivatives play a special role.

We factorize each of the two nuclear Hamiltonians $H_{a\uparrow}$ and $H_{b\downarrow}$ in Eq. (2.5),

$$H^{\mathrm{BO}}=H_{a\uparrow}\sigma_\uparrow+H_{b\downarrow}\sigma_\downarrow=(a^+a+k_a)\sigma_\uparrow+(bb^++k_b)\sigma_\downarrow. \tag{4.1}$$

The SUSY partners of $H_{a\uparrow}$ and $H_{b\downarrow}$ again are defined as

$$H_{a\downarrow}=(aa^++k_a),$$
$$H_{b\uparrow}=(b^+b+k_b). \tag{4.2}$$

Instead of z, we introduced two operators a and b. We still use z if we want to leave open whether we speak of a or b. If $z=a(b)$, then again $\overline{z}=b(a)$. To motivate the introduction of the superpartners further, we note that it is possible for special choices of f, g, and U to achieve that $H_{a\downarrow}=H_{b\downarrow}$ and $H_{b\uparrow}=H_{a\uparrow}$, so that the two BO potentials are superpartners of each other.

In Appendix A we will show that the nonadiabatic coupling can be brought in the following form:

$$H^{\mathrm{NA}}=\tilde{A}+\vec{A}+D+B_\perp+B_\parallel+C, \tag{4.3}$$

where the single terms are defined as

$$\tilde{A}:=\frac{1}{\sqrt{2}}(\sigma_-b+\sigma_+a^+)\alpha P'(x),$$
$$\vec{A}:=\frac{1}{\sqrt{2}}\alpha P'(x)(\sigma_-a+\sigma_+b^+), \tag{4.4}$$
$$D:=-\frac{1}{2}(\sigma_-W_b+\sigma_+W_a)\alpha P'(x), \tag{4.5}$$
$$C:=\frac{1}{2}\alpha P'(x)\frac{\tilde{E}_s\sigma_0-k_a\sigma_\downarrow-k_b\sigma_\uparrow}{\tilde{E}_s\sigma_0-H_{a\downarrow}\sigma_\downarrow-H_{b\uparrow}\sigma_\uparrow}\alpha P'(x), \tag{4.6}$$
$$B_\perp:=-\vec{A}R\tilde{A}, \tag{4.7}$$

and

$$B_\parallel:=-\vec{A}\frac{|s\rangle\langle s|}{\tilde{E}_s-E_s}\tilde{A}, \tag{4.8}$$

with

$$R:=\frac{\sigma_0-|s\rangle\langle s|}{\tilde{E}_s\sigma_0-H_{a\uparrow}\sigma_\uparrow-H_{b\downarrow}\sigma_\downarrow}. \tag{4.9}$$

Given two commuting operators X and Y^{-1} (the inverse of Y), we write $X/Y:=XY^{-1}=Y^{-1}X$ for the sake of a compact notation. We will set $\tilde{E}_s$ equal to the exact energy of the perturbed state. It is easy to show that from the terms into which we split the Born-Huang term, only $B_\perp$ is divergent, while $B_\parallel$ and C are well defined.

In the rest of this section, we will concentrate on the limit $\tilde{\gamma}\to 0$. We then get

$$P'(x)=\frac{1}{2}\frac{\tilde{\gamma}}{f^2(x)+\tilde{\gamma}^2}f'(x)$$

$$\sim\frac{1}{2}\frac{\gamma}{x^2+\gamma^2}$$

$$=:\frac{\pi}{2}\delta_\gamma(x), \tag{4.10}$$

where we set $\gamma=\tilde{\gamma}/f'(0)$.

In the perturbation theory the Brillouin-Wigner (BW) expression for the energy may be written as

$$\tilde{E}_s-E_s=\sum_{n=0}^{\infty}\langle s|H^{\mathrm{NA}}(RH^{\mathrm{NA}})^n|s\rangle$$

$$=\langle s|(\tilde{A}+\vec{A}+\tilde{A}R\tilde{A}+\tilde{A}R\vec{A}+\vec{A}R\tilde{A}+\vec{A}R\vec{A}$$
$$+B_\perp+B_\parallel+C+D+\mathrm{h.o.})|s\rangle. \tag{4.11}$$

To restrict the number of terms to be evaluated, we use the following attributes of the appearing operators.

(1) In the limit $\gamma\to 0$, D vanishes, as $W(0)=0$ and $W(x)$ is slowly varying, so the product with a sufficiently localized function, like $\delta_\gamma(x)$, vanishes.

(2) $\vec{A}|s\rangle=0$, for the action of an odd z operator on the—by assumption—even function $|s\rangle$ leads again to a slowly varying odd function, which is annihilated by application of the Lorentzian. Clearly $B_\parallel=0$ for this reason.

(3) The operators $\tilde{A},\vec{A}$ are odd, so they only have matrix elements between an even and an odd function. Thus, in the perturbation expression (4.11), only an even number of A operators appear. The operators $B_\perp$ and C are even, so they have only matrix elements between two-odd or two-even functions. So clearly, the perturbation series will only contain terms of even order. From the discussion in Appendix D, it further follows that actually only the matrix elements of C between even functions are not zero.

(4) For every term in the sum (4.11) containing $\vec{A}R\tilde{A}$ in some position, we can find one term differing only insofar as in this position appears the operator $B_\perp$ instead, and vice versa. Clearly, these terms cancel. This cancellation involves only terms of the same order. All terms containing $\vec{A}R\tilde{A}$ and $B_\perp$ will fall completely out of the sum. This is very satisfactory, as these terms are the only divergent expressions in the sum. We just note that this cancellation will also occur for more general Hamiltonians for which $g(x)$ is not just a constant and which need not be symmetric.

The reader may check that, up to second order, of the explicitly given terms in the last line of Eq. (4.11), only the term $\langle s|C|s\rangle$ survives. Using all these properties, we can express the perturbation series in a simpler form. With the operator F

$$F:=\sum_{m=0}^{\infty}(\vec{A}R)^{2m}C\sum_{n=0}^{\infty}(R\tilde{A})^{2n} \tag{4.12}$$

the perturbation series reads

$$\langle s|F\sum_{q=0}^{\infty}(RF)^q|s\rangle. \tag{4.13}$$

We still can further simplify this expression by introducing a state $|one\rangle$, which obeys the following two conditions: (1) $|one\rangle$ is a valid test function for Dirac's δ function, this implies that it is of bounded variation. (2) $\langle one|\delta(x)|one\rangle=1$.

Let $|n\rangle$ be a slowly varying function and $|v\rangle$ be arbitrary. Then we can find a decomposition of matrix elements involving the Lorentzian $\delta_\gamma(x)$

$$\lim_{\gamma\to 0}\langle n|\delta_\gamma(x)|v\rangle=\langle n|\delta(x)|one\rangle\lim_{\gamma\to 0}\langle one|\delta_\gamma(x)|v\rangle. \tag{4.14}$$

The functions $|one\rangle$ and $|n\rangle$ both are slowly varying, so we could introduce the δ function in the first factor. In the following, we will assume $\lim\gamma\to 0$ without making it explicit every time.

As all σ operators in Eq. (4.13) appear only in even order, we can eliminate the shift operators σ^+ and σ^-, so that we get in effect two independent equations, containing either $\sigma_\uparrow$ or $\sigma_\downarrow$, depending on the initial state $|s\rangle$. This state is characterized by the set $\{z,\zeta\}$, which is either $\{a,\uparrow\}$ or $\{b,\downarrow\}$. For the C operator, we write

$$C=\frac{1}{2}\left(\alpha\frac{\pi}{2}\right)^2\delta_\gamma\frac{\tilde{E}_s\sigma_0-k_a\sigma_\downarrow-k_b\sigma_\uparrow}{\tilde{E}_s\sigma_0-H_{a\downarrow}\sigma_\downarrow-H_{b\uparrow}\sigma_\uparrow}\delta_\gamma$$

$$=\sum_{n_z^-}\frac{1}{2}\left(\alpha\frac{\pi}{2}\right)^2\delta_\gamma|n_z^-\rangle\frac{\tilde{E}_s-k_z^-}{\tilde{E}_s-E_{n_z^-}^{\zeta}}\langle n_z^-|\delta_\gamma$$

$$=\frac{1}{2}\left(\alpha\frac{\pi}{2}\right)^2\delta_\gamma|one\rangle\sum_{n_z^-}\langle one|\delta|n_z^-\rangle$$

$$\times\frac{\tilde{E}_s-k_z^-}{\tilde{E}_s-E_{n_z^-}^{\zeta}}\langle n_z^-|\delta|one\rangle\langle one|\delta_\gamma$$

$$=\left(\alpha\frac{\pi}{2}\right)^2\frac{\tilde{E}_s-k_z^-}{2}\overline{S}\quad\delta_\gamma|one\rangle\langle one|\delta_\gamma. \tag{4.15}$$

We here introduce the two sums

$$\overline{S}=\left(\sum_{n_z^-}\frac{\langle n_z^-|\delta|n_z^-\rangle}{\tilde{E}_s-E_{n_z^-}^{\zeta}}\right),$$

$$S=\left(\sum_{n_z}\frac{\langle n_z|\delta|n_z\rangle}{\tilde{E}_s-E_{n_z}^{\zeta}}\right). \tag{4.16}$$

We note that the resolvent R defined in Eq. (4.9), appears in Eq. (4.13) sometimes ''sandwiched'' between the operators $\tilde{A}$ and $\vec{A}$. We may rewrite this similarly as

$$\tilde{A}R\vec{A}=\left(S-\frac{\langle s|\delta|s\rangle}{\tilde{E}_s-E_s}\right)\tilde{A}|one\rangle\langle one|\vec{A}. \tag{4.17}$$

Further, we write

$$|\beta| := \left|\alpha\frac{\pi}{2}\langle one|\delta_\gamma\sum_n (R\tilde{A})^{2n}|one\rangle\right| = 2\tan\left(\alpha\frac{\pi}{4}\right), \tag{4.18}$$

where the last equality will be proven in Appendix D.

Finally, we get for the perturbation series

$$\tilde{E}_s-E_s=|\beta|^2\langle s|\delta|s\rangle\frac{\tilde{E}_s-k_z^-}{2}\overline{S} \times\sum_{q=0}^{\infty}\left[|\beta|^2\frac{\tilde{E}_s-k_z^-}{2}\overline{S}\left(S-\frac{\langle s|\delta|s\rangle}{\tilde{E}_s-E_s}\right)\right]^q. \tag{4.19}$$

After summation of the geometric series, we infer an implicit expression for the energy

$$|\beta|^2\frac{\tilde{E}_s-k_z^-}{2}\overline{S}S=1. \tag{4.20}$$

We found a simple and intuitive interpretation of this formula. From Eq. (B13) it follows that the inverse of the sums (4.16) S^{-1} and $\overline{S^{-1}}$, are the logarithmic derivatives $\lambda_{z\zeta}$ and $\lambda_{z\zeta}^-$ of eigenstates $\tilde{\psi}_z^\zeta(x)$ and $\tilde{\psi}_z^{\bar{\zeta}}(x)$ of the Hamiltonians $H_{z\zeta}$ and $H_{z\zeta}^-$ at $x=0$ belonging to the energy $\tilde{E}_s$. The values of z and ζ are that of the initial state $|s\rangle$. From Appendix E, it follows

$$2(\tilde{E}_s-k_z^-)\overline{S}=\frac{\tilde{E}_s-k_z^-}{\lambda_{z\zeta}^-}=-\lambda_{z\zeta}^- =\ln[\tilde{\psi}_z^{\bar{\zeta}}(-x)]'|_{x=0}, \tag{4.21}$$

from which, together with the definition of $|\beta|$, and the energy expression (4.20), we get

$$-\frac{\lambda_{z\zeta}}{\lambda_{z\zeta}^-}=\tan^2\left(\alpha\frac{\pi}{4}\right), \tag{4.22}$$

which coincides with Eq. (3.12) or (3.13).

We want to discuss the convergence properties of the perturbation series. Clearly Eq. (3.12) is an implicit equation for the energy $\tilde{E}_s$ as a function of α. We will assume that E_s is an isolated and simple eigenvalue of $H_{a\uparrow}$, corresponding to a symmetric eigenfunction so that $\lambda_{a\uparrow}(E_s)=0$. Further E_s should not lie in the spectrum of $H_{b\downarrow}$. Then $\lambda_{b\downarrow}(E_s)$ is finite and nonzero. The left-hand-side of (3.12) is then also an analytic function of $\tilde{E}_s$ at E_s with nonvanishing first derivative. The implicit function theorem thus states that $\tilde{E}_s$ is an analytic function of α at $\alpha=0$. This implies that the Rayleigh-Schrödinger (RS) perturbation series has a nonzero radius of convergence (and obviously the BW series, too).

V. DISCUSSION

The main goal of this paper is to show that, even in situations where the electronic potential energy surfaces cross, it is possible to base a full perturbation expansion on the BO approximation. After suitable introduction of the perturbation parameter α, we succeed in showing this for systems involving only two electronic states and one nuclear coordinate. For these, we can find an equivalent diabatic representation, which allows us to solve the problem exactly for any value of α [see Eqs. (3.12) and (3.13)]. Generically, the implicit function theorem then ensures the existence of a perturbation expansion with nonzero radius of convergence.

For the special case that the problem shows a Fulton-Gouterman symmetry, we can construct the perturbation series explicitly without referring to the diabatic representation. This analysis reveals the role of the divergent terms of the nonadiabatic coupling: The most serious divergencies cancel within each order. The weakest divergencies can be treated like Dirac's δ functions and lead to a change in the boundary conditions at the locus of the intersection. Finally, in Appendix D, we show that the remaining divergences mix in states of infinitely high energy and therefore we cannot treat them like δ functions. Summation over the contribution of these high energy states leads to a renormalization of the perturbation parameter. We like to point to an analogy in a Landau-Zener-type semiclassical treatment: There, the operator x is replaced by a classical variable $x(t)=vt$, with constant velocity v. In the adiabatic representation, we get a time dependent wave function $\psi_{clas}(t)=(c_1(t),c_2(t))^T$. It is found that the modulus of the two components $c_{1,2}(t)$ will change rapidly on a scale γ/v, like the high energy states in the full quantum mechanical treatment. The NA coupling will be proportional to $\delta_\gamma(vt)$. Again, it is not allowed to replace it by a δ function.

A numerical RS calculation for near-avoided intersections would be hopeless if one had to perform summations over states of arbitrarily high energy. It seems therefore mandatory to use alternative techniques like the one proposed by Hutson and Howard [21], as actually used by Spirko *et al.* [13,14]. The perturbation scheme we used may not be the only one which will lead to regular perturbation series. Numerical evidence [13,14] indicates that the adiabatic scheme (1.4) will also lead to a regular perturbation expansion.

As we noted already, it has been questioned by many authors that a perturbation expansion based on the BO approximation can exist due to the divergence of the NA coupling. In his analysis of the problem, Wagner [12] has calculated expectation values of H^{BO}, H^D, and H^{ND} with the exact eigenfunctions of H_α at $\alpha=1$. He finds that all three contain a divergent integral, which in his mind exclude a perturbation expansion. However, in almost any perturbation

expansion, we can find matrix elements with respect to some functions that are divergent. The matrix elements of the perturbation do not need to be small as such for the perturbation expansion to be analytic, but they have to be bounded with respect to those of H_0 [22,23], that is H^{BO} in our case. In fact, the divergences in the expectation values of H^{BO}, H^D, and H^{ND} are the same for all three of them. We therefore can find a common bound for the latter two with respect to the first (To really prove the existence of a regular perturbation series we would have to show that the expectation values of the perturbation are bounded with respect to those of H^{BO} for all possible wave functions, not just with respect to the eigenfunctions of H_α.)

APPENDIX A: DECOMPOSITION OF THE HAMILTONIAN

We express the momentum operator in terms of the generalized creation and annihilation operators z,

$$p=-i(\sqrt{2}z-W_z)=-i(-\sqrt{2}z^+ +W_z). \tag{A1}$$

The nonadiabatic part of the Hamiltonian (2.8) then becomes

$$\begin{aligned} H^{NA}=&\frac{1}{2}[\alpha P'(x)]^2\sigma_0+\frac{1}{\sqrt{2}}[(\sigma_- b+\sigma_+ a^+)\alpha P'(x)\\ &+\alpha P'(x)(\sigma_- a+\sigma_+ b^+)]\\ &-\frac{1}{2}(\sigma_- W_b+\sigma_+ W_a)\alpha P'(x)\\ =&\frac{1}{2}[\alpha P'(x)]^2\sigma_0+\tilde{A}+\vec{A}+D. \end{aligned} \tag{A2}$$

As we have a perturbational treatment in mind, we extend the first term on the rhs of Eq. (A2),

$$\begin{aligned} &\frac{1}{2}[\alpha P'(x)]^2\sigma_0\\ &=\frac{1}{2}\alpha P'(x)\frac{\tilde{E}_s\sigma_0-k_a\sigma_\downarrow-k_b\sigma_\uparrow-aa^+\sigma_\downarrow-b^+b\sigma_\uparrow}{\tilde{E}_s\sigma_0-(aa^+ +k_a)\sigma_\downarrow-(b^+b+k_b)\sigma_\uparrow}\\ &\quad\times\alpha P'(x). \end{aligned} \tag{A3}$$

We now split up the quotient in Eq. (A3)

$$\begin{aligned} &\frac{1}{2}[\alpha P'(x)]^2\sigma_0\\ &=\frac{1}{2}\alpha P'(x)\frac{\tilde{E}_s\sigma_0-k_a\sigma_\downarrow-k_b\sigma_\uparrow}{\tilde{E}_s\sigma_0-H_{a\downarrow}\sigma_\downarrow-H_{b\uparrow}\sigma_\uparrow}\alpha P'(x)+\frac{1}{2}\alpha P'(x)\\ &\quad\times\frac{-aa^+\sigma_\downarrow-b^+b\sigma_\uparrow}{\tilde{E}_s\sigma_0-(aa^+ +k_a)\sigma_\downarrow-(b^+b+k_b)\sigma_\uparrow}\alpha P'(x)\\ &=C-\frac{1}{2}(\sigma_- a+\sigma_+ b^+)\alpha P'(x)\frac{\sigma_0}{\tilde{E}_s\sigma_0-H_{a\uparrow}\sigma_\uparrow-H_{b\downarrow}\sigma_\downarrow}\\ &\quad\times(\sigma_- b+\sigma_+ a^+)\alpha P'(x)\\ &=C-\vec{A}R\tilde{A}-\tilde{A}\frac{|s\rangle\langle s|}{\tilde{E}_s-E_s}\tilde{A}=C+B_\perp+B_\parallel. \end{aligned} \tag{A4}$$

We made use of the intertwining relation (C4). This splitting is allowed, because each term in the nominator of Eq. (A3) commutes separately with the denominator.

APPENDIX B: BRILLOUIN-WIGNER PERTURBATION THEORY FOR SYMMETRIC POTENTIALS WITH A DELTA PERTURBATION

In Brillouin-Wigner perturbation theory (BWPT), we start with an exact Hamiltonian $\tilde{H}$, which we split in an unperturbed Hamiltonian H and a perturbation h,

$$\tilde{H}=H+h. \tag{B1}$$

The zeroth order Hamiltonian H has a complete set of eigenfunctions $|n\rangle$, with corresponding eigenenergies E_n,

$$H|n\rangle=E_n|n\rangle, \tag{B2}$$

while we seek solutions of

$$\tilde{H}|\tilde{s}\rangle=\tilde{E}_s|\tilde{s}\rangle. \tag{B3}$$

$|\tilde{s}\rangle$ here being the exact eigenstate corresponding to the zeroth order state $|s\rangle$. In BWPT we get an implicit equation for the energy

$$\begin{aligned} \tilde{E}_s-E_s&=\langle s|h\sum_{q=0}^{\infty}\left[\sum_{n=0}^{\infty}\left(|n\rangle\langle n|\frac{1-|s\rangle\langle s|}{\tilde{E}_s-H}h\right)\right]^q|s\rangle\\ &=\langle s|h\sum_{q=0}^{\infty}(Rh)^q|s, \end{aligned} \tag{B4}$$

with the definition of the resolvent R, as in Eq. (4.9),

$$R=\frac{1-|s\rangle\langle s|}{\tilde{E}_s-H}. \tag{B5}$$

To show how BWPT works, we want to solve a simple example, the result of which will nevertheless be useful when discussing the more complex intersection problem.

We assume that the unperturbed Hamiltonian H is composed of the kinetic energy operator T and a potential V,

$$H=T+V. \tag{B6}$$

Further $V(x)$ shall be a symmetric function,

$$V(-x)=V(x). \tag{B7}$$

The perturbation is simply a multiple λ (the perturbation parameter) of a Lorentz function $\delta_\gamma(x)$ of width γ,

$$h=\lambda\,\delta_\gamma(x), \tag{B8}$$

where

$$\delta_\gamma(x)=\frac{1}{\pi}\frac{\gamma}{x^2+\gamma^2}. \tag{B9}$$

We are especially interested in $\lim_{\gamma\to 0}$. In Appendix D we show that we then may simply substitute the Lorentzian by Dirac's δ function, i.e., $h=\lambda\,\delta(x)$. We note that for slowly varying, but elsewhere arbitrary functions $|a\rangle$ and $|b\rangle$, we have the identity

$$\langle a|\,\delta|b\rangle\langle b|\,\delta|a\rangle=\langle a|\,\delta|a\rangle\langle b|\,\delta|b\rangle. \tag{B10}$$

With these specifications, Eq. (A4) reads ($|s\rangle$ is taken to be an even function)

$$\tilde{E}_s-E_s=\langle s|\lambda\,\delta|s\rangle\sum_{q=0}^{\infty}\left[\sum_{n=0}^{\infty}\left(\frac{\langle n|\lambda\,\delta|n\rangle}{\tilde{E}_s-E_n}\right)-\frac{\langle s|\lambda\,\delta|s\rangle}{\tilde{E}_s-E_s}\right]^q,$$

$$\frac{\langle s|\lambda\,\delta|s\rangle}{\tilde{E}_s-E_s}=1-\left[\sum_{n=0}^{\infty}\left(\frac{\langle n|\lambda\,\delta|n\rangle}{\tilde{E}_s-E_n}\right)-\frac{\langle s|\lambda\,\delta|s\rangle}{\tilde{E}_s-E_s}\right]. \tag{B11}$$

In the last step, we used that the sum over q forms a geometric series.

So, we get an implicit equation for the energy in dependence on the perturbation parameter λ

$$\sum_{n=0}^{\infty}\frac{\langle n|\,\delta|n\rangle}{\tilde{E}_s-E_n}=\lambda^{-1}. \tag{B12}$$

On the other hand, it is known that the logarithmic derivative of the wave function changes at $x=0$ by 2λ due to the δ-function. Keeping in mind that the wave function is symmetric we can state alternatively that

$$\frac{\psi'(0)}{\psi(0)}=\lambda. \tag{B13}$$

Here ψ is an eigenfunction of the unperturbed Hamiltonian to the energy $\tilde{E}_s$,

$$H\psi=\tilde{E}_s\psi, \tag{B14}$$

fulfilling $\psi(+\infty)=0$ (albeit for $\lambda\neq 0$, this function will not be normalizable).

In the light of this result, we may interpret Eq. (B12) as a relation of the energy of a solution of the unperturbed Schrödinger equation (B2), with its logarithmic derivative at $x=0$.

APPENDIX C: SUPERSYMMETRY

It is known that every Hamiltonian $H_{z\uparrow}$ of just one coordinate may be factorized into a product of an operator z and its Hermitian conjugate z^+ except for a constant k_z,

$$H_{z\uparrow}=-\frac{1}{2}\frac{d^2}{dx^2}+V_{z\uparrow}(x)=z^+z+k_z. \tag{C1}$$

We will write for its eigenstates $|n_z,\uparrow\rangle$, which belong to $E^{\uparrow}_{n_z}$. Further we define $k_z:=E^{\uparrow}_0$, and

$$z:=\frac{1}{\sqrt{2}}\left(W_z(x)-\frac{d}{dx}\right). \tag{C2}$$

The function $W_z(x)$ is called superpotential. Given the potential $V_{z\uparrow}(x)$, inserting Eqs. (C2) into Eq. (C1) gives a nonlinear first order differential equation, known as Riccati's equation, for $W_z(x)$. We will not have to solve this equation, but we may chose one integration constant at will. Further we can define the supersymmetric partner of the Hamiltonian $H_{z\uparrow}$ as

$$H_{z\downarrow}:=zz^+ +k_z=-\frac{1}{2}\frac{d^2}{dx^2}+V_{z\downarrow}(x), \tag{C3}$$

with the same z and k_z as in Eq. (C1). The potential $V_{z\downarrow}$ is not completely defined through $V_{z\uparrow}$ but will depend on the choice of the integration constant for W_z, too. Generally there is no distinct choice for this constant, if however $V_{z\uparrow}$ is symmetric then we may choose $W_z(0)=0$, which forces the potential $V_{z\downarrow}$ to be symmetric, too. Furthermore $W_z(x)$ will then be an antisymmetric function. From the definitions (C1) and (C3) we get the intertwining relation

$$zH_{z\uparrow}=H_{z\downarrow}z. \tag{C4}$$

Further we will make use of

$$E^{\uparrow}_{n_z+1}=E^{\downarrow}_{n_z}. \tag{C5}$$

APPENDIX D: MATRIX ELEMENTS OF OPERATORS CONTAINING A NARROW LORENTZIAN

In our perturbational expressions we have to evaluate sums over matrix elements of operators containing a Lorentzian $\delta_\gamma(x)$ in the limit $\gamma\to 0$, between eigenstates of some zeroth-order Hamiltonian, H_0. For fixed but small γ these states fall into two classes: (1) states of low energy, which vary on a length scale which is much bigger than γ; (2) states of high energy, which vary on a scale comparable to γ

or smaller. We can represent them over the width of the Lorentzian by a WKB-type expansion,

$$\psi_{n,g}(x\approx 0)\sim \sqrt{\frac{2}{\pi}}\rho_n^{-1/2}\cos[p(0)x]=:\psi_{n,g}^{\mathrm{WKB}}(x),$$

$$\psi_{n,u}(x\approx 0)\sim \sqrt{\frac{2}{\pi}}\rho_n^{-1/2}\sin[p(0)x]=:\psi_{n,u}^{\mathrm{WKB}}(x). \quad \text{(D1)}$$

Here $p(x)=\sqrt{2[E_n-V(x)]}$. For $x=0$ and $E_n\gg V(0)$ we get $p(0)\sim\sqrt{2E_n}=:p_0$ and $\rho_n=dn/dp_0$.

If we would have to deal exclusively with matrix elements between functions of the first class, we could directly replace the Lorentzian by Dirac's δ function. But even with the sum running over all intermediate states, the high-energy states may nevertheless not contribute to the sum because they may be damped sufficiently due to the energy denominators of a resolvent R like in Eq. (4.9). We will show that this holds true if the perturbation is simply proportional to $\delta_\gamma(x)$ like, e.g., in the simple example of Appendix B and also in many sums, which we discussed in the main part, but not if the Lorentzian is further multiplied with a momentum operator like in our NA coupling terms $\vec{A},\vec{A}$ in the expression β.

As an example, we analyze the situation for the problem discussed in Appendix B.

The terms in the sum (B4) we write as $\langle v|\delta_\gamma R\delta_\gamma|w\rangle$ (the functions $|v/w\rangle$ being abbreviations for the rest of the term),

$$\langle v|\delta_\gamma R\delta_\gamma|w\rangle=-\sum_n \langle v|\delta_\gamma|n\rangle\frac{1}{E_n-\tilde{E}_s}\langle n|\delta_\gamma|w\rangle. \quad \text{(D2)}$$

We want to estimate their absolute value

$$\begin{aligned}|\langle v|\delta_\gamma R\delta_\gamma|w\rangle|&=\Big|\sum_n \langle v|\delta_\gamma|n\rangle\frac{1}{E_n-\tilde{E}_s}\langle n|\delta_\gamma|w\rangle\Big|\\ &\leqslant\sqrt{\langle v|\delta_\gamma|v\rangle\langle w|\delta_\gamma|w\rangle}\sum_n\frac{\langle n|\delta_\gamma|n\rangle}{|E_n-\tilde{E}_s|},\end{aligned} \quad \text{(D3)}$$

where, in the last step, as δ_γ is a positive operator, we used the Schwarz inequality. Now we discuss the contribution of states of high energy to the sum in Eq. (D3),

$$\sum_{n>N}\frac{\langle n|\delta_\gamma|n\rangle}{|E_n-\tilde{E}_s|}\propto\int_{p_N}^{\infty}\frac{1}{p_0^2}dp_0\propto\frac{1}{p_N}, \quad \text{(D4)}$$

where we made use of Eq. (D1), to replace the sum by an integral. p_N may now be chosen so that $\lambda_N:=2\pi/p_N=\gamma\times\mathrm{const}\gg\gamma$. Then the sum over the high energy vanishes at least proportionally to γ. This effectively restricts the summation to run over the low-energy states, which are sufficiently slowly varying to allow for the introduction of the δ-function instead of the Lorentzian.

Next we will prove the identity (4.18). This can be written as

$$\beta=\left(\frac{1}{\sqrt{2}}\alpha\frac{\pi}{2}\right)^2\times\begin{cases}\langle v,a\uparrow|\delta_\gamma Ra^+\delta_\gamma Rb\,\delta_\gamma|w,a\uparrow\rangle\\ \langle v,b\downarrow|\delta_\gamma Rb\,\delta_\gamma Ra^+\delta_\gamma|w,b\downarrow\rangle.\end{cases} \quad \text{(D5)}$$

We note that the operators a^+ and b always occur in pairs, for each of them is odd. The states $|v/w,z\zeta\rangle$ are quite arbitrary and serve simply as abbreviation for the rest of the expression, but are assumed to be even. In the following, we will only consider the first alternative in Eq. (D5), for the calculation for the other choice is analogous and leads to the same result.

Let us insert an eigensystem of $H_{z\zeta}$,

$$\begin{aligned}\beta=\left(\frac{1}{\sqrt{2}}\alpha\frac{\pi}{2}\right)^2&\langle v,a\uparrow,g|\delta_\gamma\sum_n|n_a\uparrow,g\rangle\\ &\times\langle n_a\uparrow,g|\frac{1}{H_{a\uparrow}-\tilde{E}_s}a^+\delta_\gamma\sum_m|m_b\downarrow,u\rangle\\ &\times\langle m_b\downarrow,u|\frac{1}{H_{b\downarrow}-\tilde{E}_s}b\,\delta_\gamma|w,a\uparrow,g\rangle.\end{aligned} \quad \text{(D6)}$$

This can be written as

$$\begin{aligned}\beta=\left(\frac{1}{\sqrt{2}}\alpha\frac{\pi}{2}\right)^2&\langle v,a\uparrow,g|\delta_\gamma\sum_n|n_a\uparrow,g\rangle\\ &\times\frac{\sqrt{E_{n_a}^{\uparrow}}}{E_{n_a}^{\uparrow}-\tilde{E}_s}\langle(n_a-1)\downarrow,u|\delta_\gamma\sum_m|m_b\downarrow,u\rangle\\ &\times\frac{-\sqrt{E_{m_b+1}^{\downarrow}}}{E_{m_b+1}^{\downarrow}-\tilde{E}_s}\langle(m_b+1)\uparrow,g|\delta_\gamma|w,a\uparrow,g\rangle.\end{aligned} \quad \text{(D7)}$$

If we derive an upper bound for these terms, the main difference to the treatment of the term (D2), will be the appearance of an extra square root of the energy, proportional to p_0, in the numerator of an expression analogous to Eq. (D4). Instead, we would get an integral of the form $\int_{p_N}^{\infty}1/p_0dp_0$, which is logarithmically divergent. This means by no way that β does not exist, but it shows that the high energy states must be included in our analysis. Indeed, we can show that only these states contribute: The crucial point here is that the second bracket in Eq. (D7) involves the matrix element of the Lorentzian δ_γ with two odd functions. As the odd functions are clearly zero at $x=0$, this term will only then be nonvanishing, if the odd functions are both oscillating on a length-scale small compared to γ. For $\lim_{\gamma\to 0}$, we get only a contribution from the high energy states, for which the WKB expression (D1) in this limit is exact. Asymptotically, we can further replace $n\pm 1$ by n and the energies $E_{n_z}^{\zeta}$ by $p_0^2/2$. Also, it will then be correct to replace the summation over n with an integration over p_0. Now, if we regard

the WKB functions (D1) as functions of p_0 instead of n, then for every value of p_0, we have an odd and an even function. It will be advantageous, to introduce complex linear combinations of these two functions

$$\psi^{\mathrm{WKB}}_{\pm p_0} = \frac{1}{\sqrt{2}}(\psi^{\mathrm{WKB}}_{p_0,g} \pm i\psi^{\mathrm{WKB}}_{p_0,u}), \tag{D8}$$

instead.

The range of p_0 is now extended to $[-\infty,+\infty]$. We must compensate for the doubling of the integration interval by introducing an extra factor 1/2.

Asymptotically, the summations over m and n are equal, but of opposite sign. This can be written more symmetrically by writing $-1=i^2$. For symmetry reasons, only terms with an even number of summations (integrations) are nonzero, so it does no harm, to include also the terms with an odd number of summations. While, up to this point, we had to discuss the summations over n and m separately, it will now be sufficient, to discuss just one representative integral over p_0. Introducing new states $|v/w\rangle$ and changing to the position representation, we get

$$\beta = -\alpha\frac{\pi}{4}\int_{-\infty}^{+\infty} dx_1\,dx_2 \langle v|\,\delta_\gamma|x_1\rangle\langle x_2|\,\delta_\gamma|w\rangle \times \int_{-\infty}^{+\infty} dp_0 \rho_n \langle x_1|p_0,\mathrm{WKB}\rangle \frac{1}{p_0}\langle p_0,\mathrm{WKB}|x_2\rangle. \tag{D9}$$

The brackets in the integral over p_0 are just the functions (D8). The range of the integration may be taken as $[-\infty, +\infty]$, as the states with small p_0 will not contribute anyway. So, the integral over p_0 reduces to a simple Fourier integral,

$$\begin{aligned}\beta &= -\alpha\frac{\pi}{2}\int_{-\infty}^{+\infty} dx_1\,dx_2\,\psi_v^\dagger(x_1)\,\delta_\gamma(x_1)\,\delta_\gamma(x_2)\,\psi_w(x_2) \times\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{dp_0}{p_0}\exp(ip_0(x_2-x_1)) \\ &= \left(-i\alpha\frac{\pi}{2}\right)\int_{-\infty}^{+\infty} dx_1\,dx_2\,\psi_v^\dagger(x_1)\,\delta_\gamma(x_1) \times\frac{1}{2}\mathrm{sgn}(x_2-x_1)\,\delta_\gamma(x_2)\,\psi_w(x_2).\end{aligned} \tag{D10}$$

It is possible to expand the states denoted by v or w the same way, completely. We then get

$$\begin{aligned}\beta = -2i\Bigg\{ i\alpha\frac{\pi}{4} - \frac{1}{2}\sum_{n=2}^{\infty}\Bigg[\left(i\alpha\frac{\pi}{2}\right)^n \int_{-\infty}^{+\infty}\Bigg(dx_1\,\delta_\gamma(x_1) \times\int_{-\infty}^{+\infty}\Bigg\{dx_2\,\delta_\gamma(x_2)\frac{1}{2}\mathrm{sgn}(x_2-x_1)\cdots\int_{-\infty}^{+\infty}\Bigg[dx_i\,\delta_\gamma(x_i) \times\frac{1}{2}\mathrm{sgn}(x_i-x_{i-1})\cdots\int_{-\infty}^{+\infty}\Bigg(dx_n\,\delta_\gamma(x_n) \times\frac{1}{2}\mathrm{sgn}(x_n-x_{n-1})\Bigg)\cdots\Bigg]\cdots\Bigg\}\Bigg)\Bigg]\Bigg\}.\end{aligned} \tag{D11}$$

Instead of the sgn function, we can write

$$\frac{1}{2}\mathrm{sgn}(x) = \left(-\frac{1}{2}+\theta(x)\right), \tag{D12}$$

$\theta(x)$ being Heaviside's step function. If we only had a θ function instead of the sgn function, the multiple integrals for given in Eq. (D11) would be very simple. We would then integrate over a wedge-shaped region in an n-dimensional space with a symmetric integrand,

$$\int_{x_1<\cdots<x_i<\cdots<x_n}\cdots\int dx^n f(x_1)\cdots f(x_n) = \frac{1}{n!}\left(\int_{-\infty}^{+\infty} dx\,f(x)\right)^n, \tag{D13}$$

the function $f(x)$ being arbitrary. We will now introduce a short form for multiple integrals like Eq. (D13): $[1,\theta,\theta,\ldots,\theta]\equiv[1,\theta^{n-1}]$. Here, each θ stands for a whole integral $\int_{-\infty}^{+\infty}dx_i\,f(x_i)\,\theta(x_i-x_{i-1})\cdots$ and 1 for $\int_{-\infty}^{+\infty}(dx_i\,f(x_i)\cdots$. Further we set $[c,\theta^n]=c[1,\theta^n]$, where c is an arbitrary number. A number 1 or c is by no way restricted to stand in the first position, i.e., we allow also for brackets like $[a,\theta^n,b,\theta^m]$, etc., a and b again being arbitrary constants. For these multiple integrals, we now find

$$[a,\theta^n,b,\theta^m] = [a,\theta^n][b,\theta^m] \tag{D14}$$

and, using Eq. (D13),

$$\sum_{n=0}^{\infty}[a,\theta^n] = a\left\{\exp\left(\int_{-\infty}^{+\infty} f(x)\,dx\right)-1\right\}. \tag{D15}$$

In our problem, we have

$$f(x) = -i\alpha\frac{\pi}{2}\delta_\gamma(x). \tag{D16}$$

From Eq. (D12) it follows that β may be written as a sum over all possible square brackets which can be formed from inserting an arbitrary number of θ's and $-1/2$'s in each position (excluding the first, which is always occupied by $-1/2$). Tacitly assuming that this sum is convergent, we may reorder it and sum first over terms containing an equal number of $-1/2$'s, but differ in the number of θ's. In a second step, we then sum over the number of $-1/2$'s,

$$\beta=(-2i)\sum_{j=1}^{\infty}\sum_{\{n\}=\{0,\ldots,0\}}^{\{\infty,\ldots,\infty\}}\left[-\frac{1}{2},\theta^{n_1},\ldots,-\frac{1}{2},\theta^{n_j}\right]$$
$$=(-2i)\sum_{j=1}^{\infty}\left(\sum_{n=0}^{\infty}\left[-\frac{1}{2},\theta^{n}\right]\right)^{j}$$
$$=(-2i)\sum_{j=1}^{\infty}\left(-\frac{1}{2}(e^{-i\alpha\pi/2}-1)\right)^{j}$$
$$=-2i\tan\left(\alpha\frac{\pi}{4}\right). \tag{D17}$$

So we have proven Eq. (4.19).

APPENDIX E: LOGARITHMIC DERIVATIVES OF SUSY PARTNER FUNCTIONS

What is the connection between the logarithmic derivatives of a wave function $\psi^{\uparrow}$ and its SUSY partner $\psi^{\downarrow}$?

Let $\psi^{\uparrow}$ fulfill

$$c^{+}c\psi^{\uparrow}=E\psi^{\uparrow} \tag{E1}$$

and $\psi^{\downarrow}$ fulfill

$$cc^{+}\psi^{\downarrow}=E\psi^{\downarrow}. \tag{E2}$$

The two functions $\psi^{\uparrow}$ and $\psi^{\downarrow}$ are related as

$$\psi^{\uparrow}=\frac{1}{\sqrt{E}}c^{+}\psi^{\downarrow}. \tag{E3}$$

It is now straightforward to relate also the logarithmic derivatives. Again we use the idea to express the derivative through the creation operator c^{+},

$$(\ln\psi^{\uparrow})'=\frac{(\psi^{\uparrow})'}{\psi^{\uparrow}}$$
$$=\left(\frac{d}{dx}c^{+}\psi^{\downarrow}\right)\Big/\,c^{+}\psi^{\downarrow}$$
$$=[(W_c c^{+}-\sqrt{2}E)\psi^{\downarrow}]\Big/\left[\frac{1}{\sqrt{2}}\left(W_c+\frac{d}{dx}\right)\psi^{\downarrow}\right]. \tag{E4}$$

If the partner potentials are both symmetric, the superpotential W_c, will be antisymmetric. Especially $W_c(0)=0$. Then our expression simplifies further, to give

$$\ln(\psi^{\uparrow}(0))'=-2E\frac{\psi^{\downarrow}}{(\psi^{\downarrow})'}\bigg|_{x=0}=\frac{-2E}{\ln(\psi^{\downarrow}(0))'} \tag{E5}$$

or

$$\lambda_{\uparrow}=\frac{-2E}{\lambda_{\downarrow}}. \tag{E6}$$

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