Finding the unitary matrix $\mathsf{A}(x, \Delta x)$

I. DIFFERENTIAL EQUATION FOR THE MATRIX A

According to equation (63) from the paper in J. Chem. Phys. 76, 2949 (1982), the wave function at $x + \Delta x$ is related to the wave function at x by

$$\Psi(x + \Delta x) = \mathsf{A}'\Psi(x), \tag{1}$$

where $\Psi(x) = \begin{pmatrix} c_1(x) \\ c_2(x) \end{pmatrix}$ is a two-component wave function, and the matrix A' is given by the formula (65) from the paper. The formula for A-matrix is simplified after rewriting equation (1) in terms of the "flux" function $\Phi(x) = \begin{pmatrix} (p_1(x)/m)^{1/2} c_1(x) \\ (p_2(x)/m)^{1/2} c_2(x) \end{pmatrix}$:

$$\Phi(x + \Delta x) = \mathsf{A}(x, x + \Delta x)\Phi(x), \tag{2}$$

where $\mathsf{A}(x)$ is a unitary matrix that for small Δx according to equation (65) from the paper is

$$\mathsf{A}(x, x + \Delta x) = \begin{pmatrix} \exp\left(i \int_x^{x+\Delta x} p_1 dx'\right) & \lambda(x) \exp\left(i \int_x^{x+\Delta x} p_1 dx'\right) \\ -\lambda(x) \exp\left(i \int_x^{x+\Delta x} p_2 dx'\right) & \exp\left(i \int_x^{x+\Delta x} p_2 dx'\right) \end{pmatrix}, \tag{3}$$

where

$$\lambda(x) = \frac{p_1(x) + p_2(x)}{2\sqrt{p_1(x) p_2(x)}} \left[\theta(x + \Delta x) - \theta(x)\right]. \tag{4}$$

Here, we assume that the wave is propagating in positive direction (that means that momenta are positive and absolute value could be dropped), and we use units where $\hbar = 1$ (so wave numbers and momenta are the same).

Up to the first order in Δx,

$$\mathsf{A}(x, x + \Delta x) \sim \begin{pmatrix} 1 + ip_1(x)\Delta x & \tau(x)\Delta x \\ -\tau(x)\Delta x & 1 + ip_2(x)\Delta x \end{pmatrix}, \tag{5}$$

where

$$\tau(x) = \frac{p_1(x) + p_2(x)}{2\sqrt{p_1(x) p_2(x)}} \theta'(x). \tag{6}$$

Now, let us derive a differential equation for the matrix $\mathsf{A}(x_0, x)$. For this purpose, we estimate $\mathsf{A}(x_0, x + \Delta x)$ in two ways. From one side, it may be estimated by expanding in

Taylor series around the point x,

$$\mathsf{A}(x_0, x + \Delta x) \sim \mathsf{A}(x_0, x) + \Delta x\, \mathsf{A}'(x_0, x) + O(\Delta x^2), \tag{7}$$

where derivative in equation (7) is taken in respect to the second argument x. From other side, using iteration of equation (3), we obtain

$$\mathsf{A}(x_0, x + \Delta x) = \mathsf{A}(x, x + \Delta x)\mathsf{A}(x_0, x). \tag{8}$$

Using approximation (5), we obtain

$$\mathsf{A}(x_0, x + \Delta x) \sim (\mathsf{I} + i\mathsf{K}(x)\Delta x)\, \mathsf{A}(x_0, x), \tag{9}$$

where

$$\mathsf{K}(x) = \begin{pmatrix} p_1(x) & -i\tau(x) \\ i\tau(x) & p_2(x) \end{pmatrix}. \tag{10}$$

Comparing equations (7) and (9), we obtain a differential equation

$$\mathsf{A}'(x) = i\mathsf{K}(x)\mathsf{A}(x), \tag{11}$$

that should be solved with initial condition

$$\mathsf{A}(x_0) = \mathsf{I}. \tag{12}$$

In equations (11) and (12) and henceforward, we omit the first argument x_0 that is considered constant.

II. APPROXIMATE SOLUTIONS

For $x \sim x_0$, solution of equation (11) is approximated up to the term $\sim (x - x_0)$ by linear expression

$$\mathsf{A}(x) \approx \mathsf{I} + i\mathsf{K}(x_0)(x - x_0). \tag{13}$$

Notice that the matrix (13) is not strictly a unitary matrix.

More accurate approximation is given by exponential expression

$$\mathsf{A}(x) \approx \exp\left\{ i \int_{x_0}^{x} \mathsf{K}(x')dx' \right\}, \tag{14}$$

where matrix exponent is defined as

$$\exp(\mathsf{X}) = \sum_{n=0}^{\infty} \frac{\mathsf{X}^n}{n!}. \tag{15}$$

It may be proven that equation (14) is the exact solution as long as matrixes $\mathsf{K}(x')$ and $\mathsf{K}'(x')$ are commutative for $x_0 < x' < x$. In explicit form, the matrix exponent of i times any self-adjoint 2×2 matrix is (it could be found for example with use of Mathematica software)

$$\exp\left\{ i \begin{pmatrix} a & z \\ z^* & b \end{pmatrix} \right\} = e^{i\phi_+} \begin{pmatrix} \cos D + i\phi_- \frac{\sin D}{D} & iz\frac{\sin D}{D} \\ iz^* \frac{\sin D}{D} & \cos D - i\phi_- \frac{\sin D}{D} \end{pmatrix}, \tag{16}$$

where $\phi_+ = (a+b)/2$, $\phi_- = (a-b)/2$, and $D = \left(\phi_+^2 + |z|^2\right)^{1/2}$ (that is difference of the matrix eigenvalues). In order to calculate (14), one should substitute in equation (16)

$$a = \int_{x_0}^{x} p_1(x')dx', \quad b = \int_{x_0}^{x} p_2(x')dx', \quad z = i\int_{x_0}^{x} \tau(x')dx'. \tag{17}$$

III. EQUATIONS FOR PHASE FUNCTIONS

Here we express a unitary matrix A through four parameters ϕ_0, ϕ_a, ϕ_b, and β,

$$\mathsf{A}(x) = e^{i\phi_0(x)} \begin{pmatrix} e^{i\phi_a(x)}\cos\beta(x) & e^{-i\phi_b(x)}\sin\beta(x) \\ -e^{i\phi_b(x)}\sin\beta(x) & e^{-i\phi_a(x)}\cos\beta(x) \end{pmatrix}. \tag{18}$$

Equation (11) could be rewritten as $\mathsf{A}'(x)\mathsf{A}^{-1}(x) = i\mathsf{K}(x)$. Substituting here equation (18), we arrive to the matrix equation

$$\begin{pmatrix} i(\phi_0' + \phi_a'\cos^2\beta - \phi_b'\sin^2\beta) & \frac{1}{2}e^{i(\phi_a-\phi_b)}\left[2\beta' - i(\phi_a'+\phi_b')\sin 2\beta\right] \\ \frac{1}{2}e^{-i(\phi_a-\phi_b)}\left[-2\beta' - i(\phi_a'+\phi_b')\sin 2\beta\right] & i(\phi_0' - \phi_a'\cos^2\beta + \phi_b'\sin^2\beta) \end{pmatrix} = i\begin{pmatrix} p_1(x) & -i\tau(x) \\ i\tau(x) & p_2(x) \end{pmatrix}. \tag{19}$$

Equation (19) is equivalent to four coupled differential equations for functions ϕ_0, ϕ_a, ϕ_b, and β

$$\phi_0' + \phi_a'\cos^2\beta - \phi_b'\sin^2\beta = p_1, \tag{20}$$

$$\tfrac{1}{2}e^{i(\phi_a-\phi_b)}\left[2\beta' - i(\phi_a'+\phi_b')\sin 2\beta\right] = \tau, \tag{21}$$

$$\tfrac{1}{2}e^{-i(\phi_a-\phi_b)}\left[-2\beta' - i(\phi_a'+\phi_b')\sin 2\beta\right] = -\tau, \tag{22}$$

$$\phi_0' - \phi_a'\cos^2\beta + \phi_b'\sin^2\beta = p_2. \tag{23}$$

IV. UNCOUPLING THE SET OF DIFFERENTIAL EQUATIONS

A. Separation of the function ϕ_0

The sum of equations (20) and (23) is the equation $2\phi_0' = p_1 + p_2$, that has a solution

$$\phi_0(x) = \frac{1}{2}\int_{x_0}^{x} (p_1(x') + p_2(x'))dx' \tag{24}$$

that allows to un-couple the function ϕ_0 by trivial way.

Equations $\frac{1}{2}\left[(20) - (23)\right]$, $i\left[e^{-i(\phi_a-\phi_b)}(21) + e^{i(\phi_a-\phi_b)}(22)\right]$, and $\frac{1}{2}\left[e^{-i(\phi_a-\phi_b)}(21) - e^{i(\phi_a-\phi_b)}(22)\right]$ give a set of differential equations for the remaining undefined functions ϕ_a, ϕ_b, and β:

$$\phi_a' \cos^2\beta - \phi_b' \sin^2\beta = \sigma, \tag{25}$$

$$(\phi_a' + \phi_b') \sin 2\beta = 2\tau \sin(\phi_a - \phi_b), \tag{26}$$

$$\beta' = \tau \cos(\phi_a - \phi_b), \tag{27}$$

where $\sigma = \frac{1}{2}(p_1 - p_2)$.

Equations (25) - (27) are re-written in terms of functions $\phi_\pm = \phi_a \pm \phi_b$ as

$$\phi_-' + \phi_+' \cos 2\beta = 2\sigma, \tag{28}$$

$$\phi_+' \sin 2\beta = 2\tau \sin\phi_-, \tag{29}$$

$$\beta' = \tau \cos\phi_-. \tag{30}$$

B. Eliminating the function ϕ_+

Combining the equation $[(28) - \cot 2\beta(29)]$ with equation (30), we obtain a set of equations for only *two* unknown functions, ϕ_- and β,

$$\phi_-' = 2(\sigma - \tau \sin\phi_- \cot 2\beta), \tag{31}$$

$$\beta' = \tau\cos\phi_-. \tag{32}$$

The remaining unknown function ϕ_+ could be determined from equation (29) as

$$\phi_+(x) = 2\int_{x_0}^{x} \tau(x')\frac{\sin\phi_-(x')}{\sin 2\beta(x')}\, dx'. \tag{33}$$

V. UNCOUPLING DIFFERENTIAL EQUATIONS (31) AND (32)

Generally, uncoupling equations (31) and (32) seems to be impossible. Notice however, that setting $\tau = 0$ in equation (31), we arrive to a set of equations

$$\phi'_- = 2\sigma, \tag{34}$$

$$\beta' = \tau \cos\phi_-, \tag{35}$$

that are no longer coupled. Solution of equations (34) and (35) is

$$\phi_-(x) \equiv \phi_0(x) = 2\int_{x_0}^{x} \sigma(x')\, dx', \tag{36}$$

$$\beta(x) \equiv \beta_0(x) = \int_{x_0}^{x} \tau(x') \cos\left(2\int_{x_0}^{x'} \sigma(x'')\, dx''\right) dx'. \tag{37}$$

The obtained result for the function β, equation (37), is identical to the "phase corrected" approximation of the paper in J. Chem. Phys. 119, 11048 (2003), see equation (32) in the mentioned paper. Notice that the function β was labelled in the paper as "γ" that follows from comparison of equation (18) with the form of A-matrix adopted in this paper, see their equations (38a) - (38d). Comparison of the result for the function ϕ_-, equation (36), with the result of the mentioned paper could not be done directly, because the function ϕ_- was not derived in this paper explicitly.

To improve approximation given by equations (36) and (37), one could introduce a dummy coupling parameter g and re-write $\tau(x)$ as $g\tau(x)$ in equation (31). In final results, the parameter g should be substituted by one. Within this approach, we solve perturbatively a "weakly" coupled set of differential equations,

$$\phi'_- = 2(\sigma - g\tau \sin\phi_- \cot 2\beta), \tag{38}$$

$$\beta' = \tau \cos\phi_-. \tag{39}$$

Solution of equations (38) and (39) is searched in the form of perturbation expansion

$$\phi_- = \phi_0 + g\phi_1 + g^2\phi_2 + \ldots, \tag{40}$$

$$\beta = \beta_0 + g\beta_1 + g^2\beta_2 + \ldots, \tag{41}$$

with zero-order approximation given by equations (36) and (37).

Equations for the first-order functions are

$$\phi_1' = -2\tau \sin\phi_0 \cot 2\beta_0, \tag{42}$$

$$\beta_1' = -\tau\phi_1 \sin\phi_0. \tag{43}$$

Solution of equations (42) and (43) are expressed through zero-order approximation, equations (36) and (37) as

$$\phi_1(x) = -2\int_{x_0}^{x} \tau(x') \sin\phi_0(x') \cot 2\beta_0(x')\, dx', \tag{44}$$

$$\beta_1(x) = 2\int_{x_0}^{x} \tau(x') \sin\phi_0(x') \left(\int_{x_0}^{x'} \tau(x'') \sin\phi_0(x'') \cot 2\beta_0(x'')\, dx''\right) dx'. \tag{45}$$

The approximation $\phi_- \approx \phi_0 + \phi_1$, $\beta \approx \beta_0 + \beta_1$ is expected to be superior to the "phase corrected" approximation, on expense of involving more integrals.

If we assume that all trigonometric functions in equations (44) and (45) are of order of one (it may be not true however for $\cot 2\beta$), then it could be seen from comparison with equations (36) and (37) that $\phi_1 \ll \phi_0$ and $\beta_1 \ll \beta_0$ if $\tau \ll \sigma$. It is always true if mass is large, or $\hbar$ small (when using units of unit mass instead of unit $\hbar$). An exception is very sharp avoided-crossing, when τ could have large peak.

Finally, it could be mentioned that a simultaneous limit of $\tau \to 0$ in equations (31) and (32) is undefined because of a singular term $\cot 2\beta$ in r.h.s. of equation (31) that is undefined at $\tau \to 0$.

VI. EXPANSIONS IN POWERS OF Δx

Here, we assume that matrix elements of the potential could be expanded in Taylor series

$$v_{ij}(x) = \sum_{n=0}^{\infty} v_{ij}^{(n)} (x - x_0)^n. \tag{46}$$

Then, the functions σ and τ could be expanded in power series

$$\sigma(x) = \sum_{n=0}^{\infty} \sigma_n (x - x_0)^n, \tag{47}$$

$$\tau(x) = \sum_{n=0}^{\infty} \tau_n (x - x_0)^n, \tag{48}$$

using formulas

$$\sigma = \frac{1}{2}\left(\mathrm{Tr}\mathsf{W} - 2\mathrm{Det}^{1/2}\mathsf{W}\right)^{1/2}, \tag{49}$$

$$\tau = \frac{(v_{11}-v_{22})v'_{12} - (v'_{11}-v'_{22})v_{12}}{(v_{11}-v_{22})^2 + 4v_{12}^2}, \tag{50}$$

where $\mathsf{W} = [2m(E\mathsf{I} - \mathsf{V})]^{1/2}$.

After substitution of equations (47) and (48) into (25) - (27) and solving resulting equations in each order in $\Delta x = x - x0$, we finally obtain

$$\phi_a = \sigma_0\Delta x + \tfrac{1}{2}\sigma_1\Delta x^2 + \tfrac{1}{3}(\sigma_2 + \sigma_0\tau_0^2)\Delta x^3 + (\tfrac{1}{4}\sigma_3 + \tfrac{1}{6}\sigma_1\tau_0^2 + \tfrac{1}{3}\sigma_0\tau_0\tau_1)\Delta x^4 + \ldots, \tag{51}$$

$$\phi_b = \frac{\sigma_0\tau_1 - \sigma_1\tau_0}{6\tau_0}\Delta x^2 + \frac{-2\sigma_2\tau_0^2 + \sigma_1\tau_0\tau_1 - \sigma_0\tau_1^2 + 2\sigma_0\tau_0\tau_2}{12\tau_0^2}\Delta x^3 + \frac{P_4}{360\tau_0^3}\Delta x^4 + \ldots, \tag{52}$$

$$\beta = \tau_0\Delta x + \tfrac{1}{2}\tau_1\Delta x^2 + \tfrac{1}{6}(-\sigma_0^2\tau_0 + 2\tau_2)\Delta x^3 + \tfrac{1}{12}(-2\sigma_0\sigma_1\tau_0 - \sigma_0^2\tau_1 + 3\tau_3)\Delta x^4 + \ldots, \tag{53}$$

where

$$P_4 = -4\sigma_0^2\sigma_1\tau_0^3 - 54\sigma_3\tau_0^3 - 4\sigma_1\tau_0^5 + 18\sigma_2\tau_0^2\tau_1 + 4\sigma_0\tau_0^4\tau_1 - 15\sigma_1\tau_0\tau_1^2 + 15\sigma_0\tau_1^3 + 32\sigma_1\tau_0^2\tau_2 - 50\sigma_0\tau_0\tau_1\tau_2 + 54\sigma_0\tau_0^2\tau_3. \tag{54}$$

Numerically it is feasible to calculate hundreds of expansion coefficients for a given value of x_0.

Let us compare small-Δx approximation with the small coupling approximation for the function β, see equation (37). Repeating derivations with an arbitrary coupling parameter g that was introduced in equation (40), we obtain

$$\beta = \tau_0\Delta x + \tfrac{1}{2}\tau_1\Delta x^2 + \frac{-2\sigma_0^2\tau_0 + (1+g)^2\tau_2}{3(1+g)^2}\Delta x^3 + \ldots. \tag{55}$$

It follows from equation (55) that $g \to 0$ limit, equation (37), is accurate up to the second order in Δx.

VII. NUMERICAL EXAMPLE

We use the same example of vector potential as in the paper of M. F. Herman and M. P. Moody "Numerical Study ...", 2005,

$$\mathsf{V}(x) = \begin{pmatrix} \tanh(x-2)\tanh(x+2) & 0.1\exp(-0.05x^2) \\ 0.1\exp(-0.05x^2) & -\tanh(x-2)\tanh(x+2) \end{pmatrix}, \tag{56}$$

$E = 2.8$, and $m = 1836$. Crossing of eigenvalues of the potential occurs at $x = \pm 2.001 \pm 0.082i$, so there is a pair of sharp avoided-crossings at $x \approx \pm 2$, see Fig. 1.

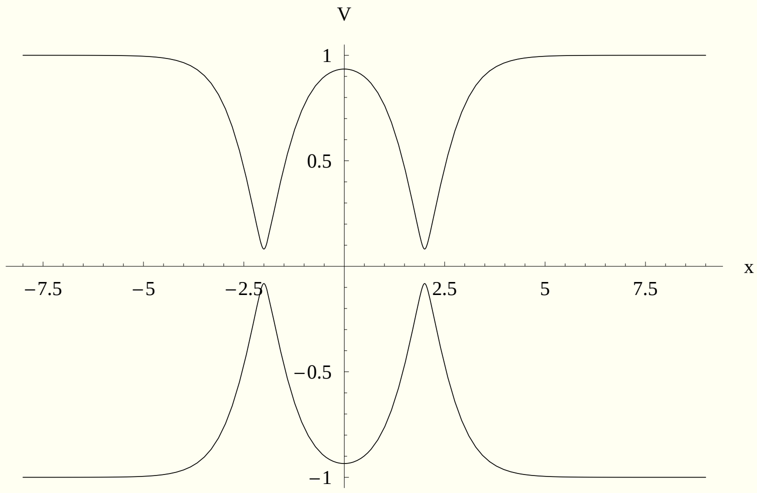

FIG. 1. Adiabatic potentials for the example (56)

A. Accuracy of small-coupling approximation

Here we compare exact solutions of differential equations (31) and (32) with the small-coupling limit, equations (36) and (37). Comparison is done in thee regions, far from avoided-crossings ($x_0 = -8$), at avoided crossing ($x_0 = -2$), and in the intermediate region ($x_0 = -3$), see figures (2), (3), and (4).

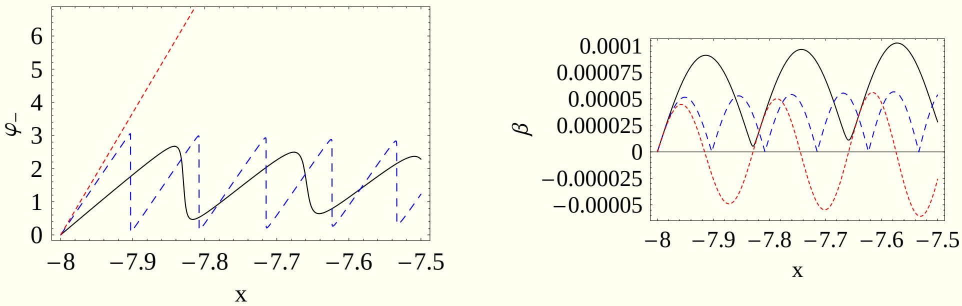

FIG. 2. Phase $\phi_-(x)$ and the function $\beta(x)$, when the starting point $x_0 = -8$ is far from avoided-crossing, left and right sides respectively. Solid curves are found by numerical solution of differential equations (31) and (32). Dashed curves are solutions in small-coupling regime, namely solutions of differential equations (38) and (39) at $g = 0.15$. Dotted curves are solutions of uncoupled equations (34) and (35) that could be found in quadratures, equations (36) and (37).

Results show that small-coupling approximation is accurate within several percent in the most important area of avoided-crossing, when the interval Δx is smaller than ~ 0.2. In the areas away from avoided-crossings, the approximation is not accurate unless Δx is smaller than ~ 0.03. Nevertheless, since these areas give small contributions to the

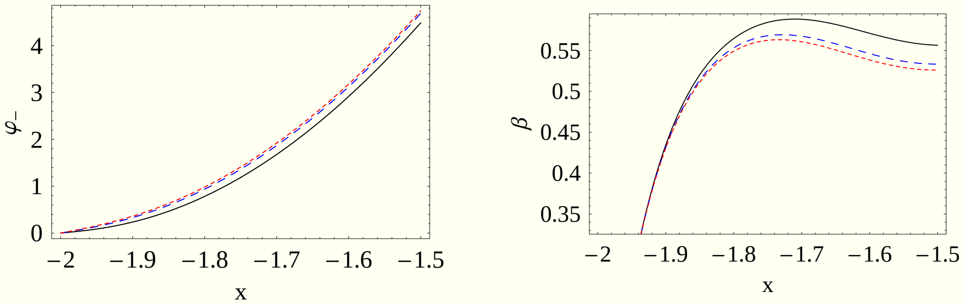

FIG. 3. Phase $\phi_-(x)$ and the function $\beta(x)$, when $x_0 = -2$ is near the avoided-crossing.

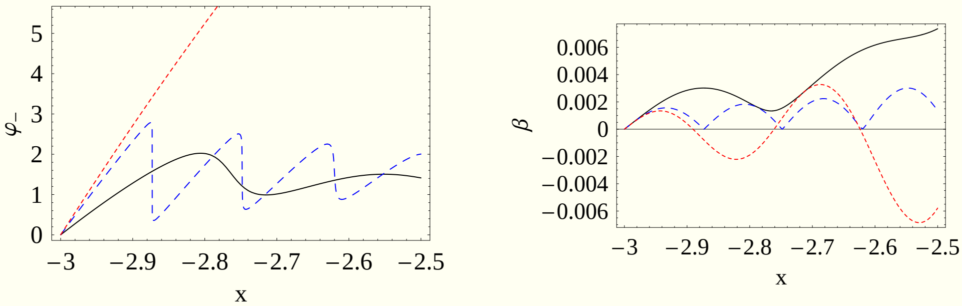

FIG. 4. Phase $\phi_-(x)$ and the function $\beta(x)$, when $x_0 = -3$.

transition rate (small change of the angle β), we could expect that overall result of matrix multiplications will be accurate when $\Delta x < 0.2$. Figures 2 and 4 show a sequence of "avoided-crossing" points, where the functions are near-singular in small-coupling regime. It is the effect of a singular term $\cot 2\beta$ in equations. When g is small, but non-zero, the solution is a continuous "adiabatic" curve, but when $g = 0$, the singular term disappears, and solution chooses "diabatic" curve. As a result, a better approximation for non-zero g would be a discontinuous branch of solutions of equations (34) and (35) selected so that $0 < \phi_- < \pi$, $\beta > 0$.

B. Accuracy of small-Δx approximation

Here we compare exact functions ϕ_- and β with sum of the small-Δx expansions, equations (51) - (53). To accelerate convergence, Pade approximant technique was used. Results are shown in figures (5), (6), and (7).

Sum of 30 coefficients is usually accurate up to $\Delta x \sim 0.3$, with exception of $x_0 = -8$, where transition rate is negligibly small. However, this method requires large number of

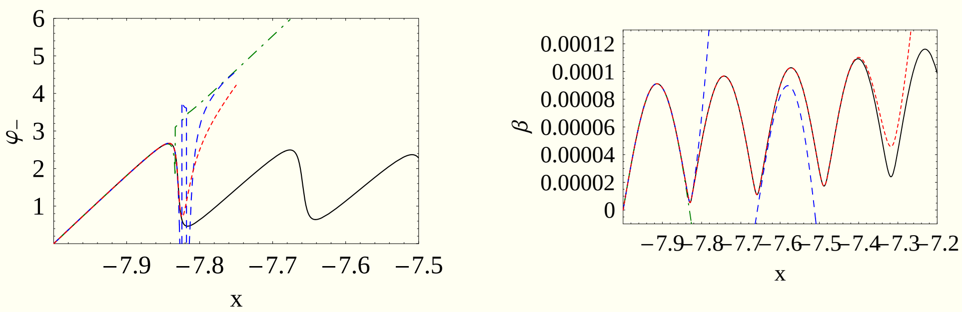

FIG. 5. Phase $\phi_{-}(x)$ and the function $\beta(x)$, when the starting point $x_0 = -8$ is far from avoided-crossing, left and right sides respectively. Solid curves are found by numerical solution of differential equations (31) and (32). Results of summation of 10, 30, and 100 coefficient of series in Δx are shown as dot-dashed, dashed and dotted lines respectively.

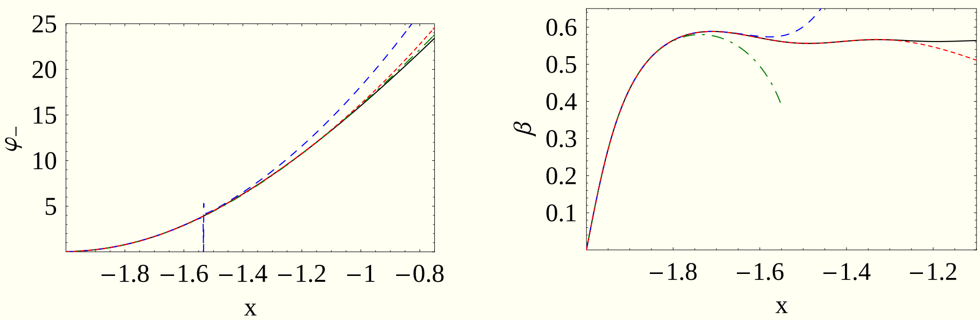

FIG. 6. The same as Fig. 5, but at $x_0 = -2$ near avoided-crossing.

derivatives of the potential, that could not be available for potential found numerically or from an experiment.

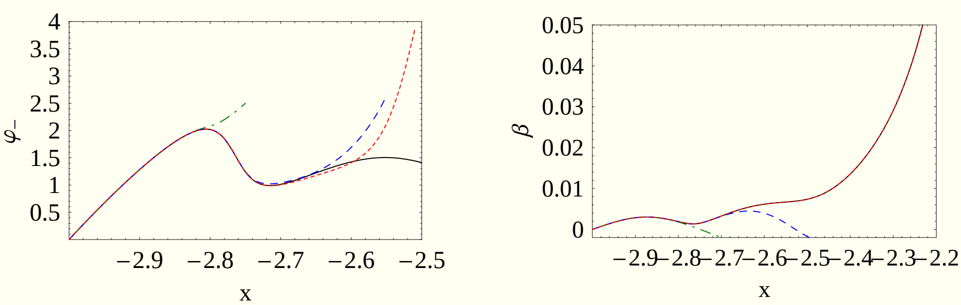

FIG. 7. The same as Fig. 5, but at $x_0 = -3$. Dotted and solid curves practically undistinguished up to $x = -2.1$.