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Brillouin-Wigner perturbation methods for coupled oscillators

V. Špirko,[1,2] M. Rozložník,[2] and J. Čížek[1,2]
[1]University of Waterloo, Department of Applied Mathematics, Waterloo, Ontario, Canada N2L 3G1
[2]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

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We study the use of Brillouin-Wigner perturbation theory (BWPT) coupled with Padé approximant summation techniques to solve problems formulated as coupled (diabatic, adiabatic, ''mixed'') channels. Several iterative BWPT schemes are examined. BW perturbation series demonstrate better convergence properties, making them more practical and efficient than traditional Rayleigh-Schrödinger perturbation series.

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There are many quantum-mechanical problems involving distinctive groups of dynamical variables which may be approached using the formalism of the so-called adiabatic separation. The separation rests on the approximation that the motion associated with one group of variables, say **r**, may be be treated as if other variables, say **R**, were frozen. Under this condition, it is convenient to express the total wave function of the studied problem as a product of a function depending only on the **R** variables and a function depending explicitly on the **r** variables, but only parametrically on the **R** variables, i.e.,

$$\psi^0(\mathbf{r},\mathbf{R})=\varphi(\mathbf{r};\mathbf{R})\chi(\mathbf{R}). \tag{1}$$

Relying on this factorization allows one to solve the **r**-dependent dynamical subproblem separately for each set of the ''parameters'' **R** so that the corresponding eigenvalues form effective potential energy functions for the **R**-dependent dynamical subproblems (for each ''**r** state'' there is a separate **R**-dependent potential energy function) and the derivatives of the corresponding wave functions with respect to **R**, the so-called nonadiabatic corrections, describe the dynamical coupling between the **R** and **r** motions. In some cases the corrections are found negligible, and the whole dynamical problem thus separates into two much less demanding subproblems.

A very important subset of the discussed problems involves factorization of the total wave function with respect to a single variable, say R, so that the treatment leads generally to the solution of a system of (coupled) ordinary Schrödinger equations and, in the last step, i.e., in the adiabatic (Born-Oppenheimer) approximation, even to the solution of single one-dimensional Schrödinger equations. The latter problems are both easily solvable and very useful for gaining insight. Nevertheless, they do not provide quantitative results; to obtain these, one should account for the nonadiabatic couplings.

Usually, the nonadiabatic corrections are small, and so are well suited to calculation by perturbation theory. Probably the best-suited perturbative approach in this direction has been suggested by Hutson and Howard [1]. This approach has been thoroughly tested, within the framework of the Rayleigh-Schrödinger perturbation theory, on a system of two anharmonically coupled oscillators, and found fairly adequate for relatively isolated states of moderately coupled oscillators [2]. In the case of stronger couplings, especially in the case of closer coincidences of the adiabatic states, the perturbation series either converged slowly or failed to converge completely. Many of these series, however, have been found summable, highly accurately, by means of Padé approximants [3]. High accuracy of the Padé approximant summation of the perturbation series has also been found in the case of Morse oscillators [4]. But, due to numerical singularities in the differential equations for the perturbation corrections, the approach collapses in the case of accidentally coinciding adiabatic energy levels.

To remove these perturbation ''resonances,'' the approach has recently been generalized [5] by introducing the so-called ''mixed'' representations which arise from the diabatic representation of a given problem

$$\mathbf{H}^d=-\frac{1}{2\mu}\frac{d^2}{dR^2}\mathbf{I}+\mathbf{V}^d(R) \tag{2}$$

($\mathbf{I}$ and μ being the unit matrix and reduced mass, respectively) by performing unitary transformations on the pertinent diabatic potential energy matrix,

$$\mathbf{V}^\alpha=\mathbf{S}^{-1}(R)\mathbf{V}^d\mathbf{S}(R). \tag{3}$$

The *mixed* representations acquire the following form:

$$\mathbf{H}^\alpha=-\frac{1}{2\mu}\frac{d^2}{dR^2}\mathbf{I}+\mathbf{V}^\alpha(R)+\mathbf{G}^\alpha(R)+2\mathbf{F}^\alpha\frac{d}{dR}, \tag{4}$$

where the generalized coupling terms $\mathbf{G}^\alpha$ and $\mathbf{F}^\alpha$ are given as

$$\mathbf{F}^\alpha=-\frac{1}{2\mu}\mathbf{S}^{-1}(R)\frac{d}{dR}\mathbf{S}(R) \tag{5}$$

and

$$\mathbf{G}^\alpha=-\frac{1}{2\mu}\mathbf{S}^{-1}(R)\frac{d^2}{dR^2}\mathbf{S}(R). \tag{6}$$

Obviously, the adiabatic representation is obtained as a special case with purely diagonal potential energy matrix $\mathbf{V}^\alpha$.

Different representations provide different zeroth order eigenvalues and eigenvectors. Thus, in principle, switching from a given representation to another one may remove accidental energy resonances (i.e., numerical singularities in the pertinent perturbation equations), and may be thus used to improve the accuracy and stability of the perturbation calculations, especially in the case of closely coinciding energy levels. The approach has been probed by actual calculations with realistic models for two interacting states exhibiting avoided crossings, and, highly accurate results have been obtained for all the probed energy levels. Nevertheless, for several of these levels the perturbation series diverged so strongly that their accurate summation required working with very high-accuracy arithmetic (the actual series were processed using the symbolic language MAPLE [6]).

A possible alternative to the suggested Rayleigh-Schrödinger (RS) approach to the perturbational calculations is to use the Brillouin-Wigner (BW) perturbation theory [7]. Unlike the RS approach, the BW approach accounts for the contribution to the correction function from the reference state and thus may be expected to have a larger radius of convergence than that of the RS approach and, consequently, less ‘‘prohibitive’’ requirements. In the BW treatment of our problem, the exact wave functions, $\Psi_{jn}(\mathbf{r},R)$, and energies E_{jn}, satisfy the following perturbation equation:

$$(E_{jn}-\mathbf{H}^0)\Psi_{jn}(\mathbf{r},R)=\mathbf{H}'\Psi_{jn}(\mathbf{r},R), \tag{7}$$

where

$$\mathbf{H}^0\{\chi_{jn}(R)\varphi_j(\mathbf{r};R)\}=\mathbf{H}^0_{jj}\{\chi_{jn}(R)\}\varphi_j(\mathbf{r};R) \tag{8}$$

and

$$\mathbf{H}'\{\chi_{jn}(R)\varphi_j(\mathbf{r};R)\}=\sum_{i\neq j}\mathbf{H}'_{ji}\{\chi_{jn}(R)\}\varphi_j(\mathbf{r};R), \tag{9}$$

and the eigenfunctions $\Psi_{jn}(\mathbf{r},R)$ are assumed to be expressed as the following sums:

$$\Psi_{jn}(\mathbf{r},R)=\psi^0_{jn}(\mathbf{r},R)+\Phi_{jn}(\mathbf{r},R), \tag{10}$$

where the unknown (correction) functions $\Phi_{jn}(\mathbf{r},R)$ are orthogonal to the $\psi^0_{jn}(\mathbf{r},R)$ functions from Eq. (1).

The correction functions may be expressed as the following expansions:

$$\Phi_{jn}(\mathbf{r},R)=\sum_{k=0}\varphi_k(\mathbf{r};R)C_{jn;k}(R), \tag{11}$$

where the unknown expansion coefficients $C_{jn;k}$ satisfy the following implicit equations (for details see Ref. [7]):

$$[E_{jn}-H^0_{mm}]C_{jn;m}(R)=[(1-\delta_{jm})H'_{jm}-E'_{jn}\delta_{jm}]\chi_{jn}(R)+\sum_{k\neq m}H'_{km}\{C_{jn;k}(R)\} \tag{12}$$

and where

$$E'_{jn}=\sum_{i\neq j}\langle H'_{ji}\{\chi_{jn}(R)\},C_{jn;i}(R)\rangle_R. \tag{13}$$

To solve Eq. (12), two iterative schemes have been suggested in the literature [7]:

$$[E^{(p)}_{jn}-H^0_{mm}]C^{(p+1)}_{jn;m}=[(1-\delta_{jm})H'_{jm}-E'^{(p)}_{jn}\delta_{jm}]\chi_{jn}(R)+\sum_{k\neq m}H'_{km}\{C^{(p)}_{jn;k}(R)\} \tag{14}$$

and

$$\begin{aligned}[E^{(p)}_{jn}-H^0_{mm}]C^{(p+1)}_{jn;m}&=[(1-\delta_{jm})H'_{jm}-E'^{(p)}_{jn}\delta_{jm}]\chi_{jn}(R)\\&\quad+\sum_{k>m}H'_{km}\{C^{(p+1)}_{jn;k}(R)\}\\&\quad+\sum_{k<m}H'_{km}\{C^{(p)}_{jn;k}(R)\},\end{aligned} \tag{15}$$

where

$$E^{(p+1)}_{jn}=E^0_{jn}+\sum_{i\neq j}\langle H'_{ji}\{\chi_{jn}(R)\}C^{(p+1)}_{jn;i}(R)\rangle_R. \tag{16}$$

The latter scheme was found in Ref. [7] to provide better convergence. However, in the course of iterating the correction functions $C^{(p)}_{jn,k}(R)$ become nonorthogonal with respect to the functions $\chi_{jn}(R)$ and, to keep calculations numerically stable, the orthogonality should be reestablished at each iteration step.

Usually, both schemes, say BW$_1$ and BW$_2$, provide oscillating corrections. Thus, a more rapid convergence may be expected for the following modification of the iterative schemes (it gives rise to the BW$_3$ and BW$_4$ schemes):

$$2E^{(p+1)}_{jn}=E^{(p)}_{jn}+E^0_{jn}+\sum_{i\neq j}\langle H'_{ji}\{\chi_{jn}(R)\}C^{(p+1)}_{jn;i}(R)\rangle_R. \tag{17}$$

To get insight into the practical prospects of the discussed BW approach, and to compare it with the previously used RS approach, we have performed the same model calculations as in our previous studies [3–5]. Namely, we have considered a set of problems for the following Hamiltonians [3,4]:

$$\mathbf{H}^a=-\frac{1}{2}\frac{\partial^2}{\partial x^2}+\frac{1}{2}\omega_x^2-\frac{1}{2}\frac{\partial^2}{\partial y^2}+\frac{1}{2}\omega_y^2+\alpha x^2y^2, \tag{18}$$

$$\begin{aligned}\mathbf{H}^b=&-\frac{\partial^2}{\partial x^2}+V_x(1-\exp[-\omega_x x])^2-\frac{\partial^2}{\partial y^2}\\&+V_y(1-\exp[-\omega_y y])^2+V_{xy}(1-\exp[-\omega_x x])\\&\times(1-\exp[-\omega_y y]),\end{aligned} \tag{19}$$

and the ‘‘diabatic’’ problem from [5] with parameters taken from Ref. [8]:

TABLE I. Brillouin-Wigner energy estimates for the [0,2] and [2,0] states of the $\mathbf{H}^a$ Hamiltonian. Case C (N_{BW_i} is the number of iterations necessary to get eigenvalues accurate to one part in 10^8 in the ith BW iterational scheme; integers given in parentheses give the degrees of the diagonal Padé approximants which are necessary to get the same accuracy in the case of diverging, or very slowly converging, perturbation series).

α	N_{BW_1}	N_{BW_2}	N_{BW_3}	N_{BW_4}	$E(\mathrm{BW})$
			State [0,2]		
0.3	176	40	34	15	3.18300240
0.7	182	22	40	17	3.36332862
1.1	264	16	58	19	3.50966275
			State [2,0]		
0.5	89	(10)	17	15	3.51563617
0.9	68	(12)	27	13	3.75859467
1.3	56	(9)	46	15	3.94960343

$$\mathbf{H}^c=\begin{pmatrix} -\dfrac{1}{2\mu}\dfrac{d^2}{dR^2}+V_{11}(R) & V_{12}(R) \\ V_{21}(R) & -\dfrac{1}{2\mu}\dfrac{d^2}{dR^2}+V_{22}(R) \end{pmatrix}. \tag{20}$$

According to the actual calculations (performed in the adiabatic representation for $\mathbf{H}^a$ and $\mathbf{H}^b$ and in the *mixed* representations for $\mathbf{H}^c$), the BW approach appears to be numerically superior to the RS approach.

(1) Similarly to the RS approach, it provides highly accurate results for all the levels which are away from any accidental ‘‘resonances’’ with other levels, even in the case of strong and very strong perturbation couplings; the convergence of the perturbation series may be efficiently accelerated using the Padé approximant summation technique (see Table I).

(2) Unlike the RS approach, in the cases of two closely coinciding levels it either converges safely or provides asymptotic perturbation series that are accurately summable (see Tables II and III). The perturbation series exhibit profound dependence on the ‘‘zeroth order’’ energy estimates and it may be used to improve their summabilities especially in the case of the BW_1 and BW_3 schemes. The only limiting problem arises due to the fact that, in the case of exactly coinciding states, the iteration processes may converge to only one of the two sought eigenvalues.

TABLE II. Brillouin-Wigner estimates of the energies of the adiabatically crossing levels of the **H** (N_{BW_i} is the number of iterations necessary for to get eigenvalues accurate to one part in 10^8 in the ith BW iterational scheme) Hamiltonian.

α	N_{BW_2}	N_{BW_3}	N_{BW_4}	$E(\mathrm{BW})$
		Case A: State [0,5]		
0.2	193	19	15	4.93170392
0.214585	[a]	39	34	4.96151640
0.25	46	18	13	5.03386237
		Case A: State [2,1]		
0.2	29	19	13	4.86125864
0.214585	78	35	32	4.88635244
0.25	20	15	15	4.94184811

[a] Converging, from a broad set of estimates, to the value assigned to the [2,1] state.

TABLE III. Brillouin-Wigner perturbation series for the [1,2] state of the $\mathbf{H}^b$ Hamiltonian (Case A; $V_{xy}=-150$) (BW_i is the BW iteration scheme used to get the particular corrections).

Order	BW_1	BW_1	BW_2	BW_2
i	12	7	8	7
$[i/i]$	552.951080	552.951074	552.951074	552.951074
$[i/i+1]$	552.951073	552.951074	552.951074	552.951074

(3) It appears also that the BW approach may efficiently work even in the case of multiple energy intercrossings where the RS approach fails completely; for instance, in the case of the [3,6], [5,3], and [6,2] states of the Hamiltonian $\mathbf{H}^a$ (the degree of coincidence of these states may be seen in Fig. 3 of Ref. [3]). In the case of the two last states, the BW approach (especially the BW_2 and BW_4 schemes) provides strongly converging series for a wide range of values of the coupling constant α, and, in the case of the [3,6] state, it gives very accurately summable asymptotic series (see Table IV).

The performance of the BW approach may also be improved using the *mixed* representations. As a matter of fact, the approach has allowed very accurate determination of all the probed states of the Hamiltonian $\mathbf{H}^c$. Although most of the sought energies were obtainable within the framework of the adiabatic representation, in some cases, such as in the case of the three lowest $[0,i]$ states, we had to go beyond its scope (see Table V).

Unlike the standard variational approaches, the perturbation procedure accounts automatically for contributions from the continuum states and yields energy corrections directly in terms of the relevant quantum numbers. Thus, the procedure appears as a promising tool for a broad class of practical applications. For instance, it may be used to evaluate (and directly assign) all reasonably isolated states of the light, loosely bound molecular complexes. Recently, the procedure has provided very accurate energies and unambiguous as-

TABLE IV. Brillouin-Wigner perturbation series for the [3,6] state of the $\mathbf{H}^a$ Hamiltonian [Case A (BW_i is the BW iteration scheme used to get the particular corrections)].

Order	$\alpha=0.4(\mathrm{BW}_2)$	$\alpha=0.5(\mathrm{BW}_4)$	$\alpha=0.6(\mathrm{BW}_2)$
i	9	8	11
$[i/i]$	13.39062451	13.62422204	14.52530711
$[i/i+1]$	13.39062451	13.62421907	14.52530711
Var[a]	13.390625	13.624224	14.525322

[a] Variational calculation with a basis set of 900 functions.

TABLE V. Estimates of the $[0,i]$ eigenvalues of the Hamiltonian $\mathbf{H}^c$ [A_i is the value of the rotational parameter A providing optimal convergence of the perturbation series (see Ref. [5]); N_i is the number of iterations necessary to get eigenvalues accurate to one part in 10^8 in the ith BW iterational scheme; P_i is the degree of the diagonal Padé approximant necessary to get eigenvalues accurate to one part in 10^8].

State	Energy	A_2	N_2	P_2	A_4	N_4	P_4
[0,0]	−0.65249310	0.32	23	10	0.32	23	9
[0,1]	−0.63739737	1.63	25	8	1.65	23	8
[0,2]	−0.62356479	1.64	[a]	7	0.36	[a]	18
[0,3]	−0.60788555	1.10	[a]	9	1.08	[a]	6
[0,4]	−0.59604250	1.09	[a]	9	1.00	[a]	7

[a] Converging, but not converged for $N<40$.

signment of all the bound vibrational states of the Na..FH van der Waals molecule in a full accord with a large scale variational calculation [9]. In some favorite situations, such as the one illustrated by Fig. 1, the procedure may even allow for evaluation of the positions and lifetimes of the quasibound states by means of the stabilization method [10]. Though the ''periodic'' discontinuities in the stabilization diagrams (arising due to mathematical singularities in the perturbation equations) can make these diagrams incomplete, the ''incomplete'' diagrams may still provide sufficiently accurate estimates of the sought characteristics. Interestingly, positions of the discontinuities differ for different mixed representations.

Of course, despite its promising features, the suggested BW approach is not free of all the typical drawbacks of the perturbation theory. Apart from the obvious fact that it is not suitable for describing clusters of closely coinciding states, its usefulness is limited mostly by the fact that there is no general procedure which would allow evaluation of accurate wave functions from diverging perturbation series [11]. The latter problem and the phenomenon of the ''periodic'' discontinuities in the stabilization diagrams are scheduled to be addressed in our future studies.

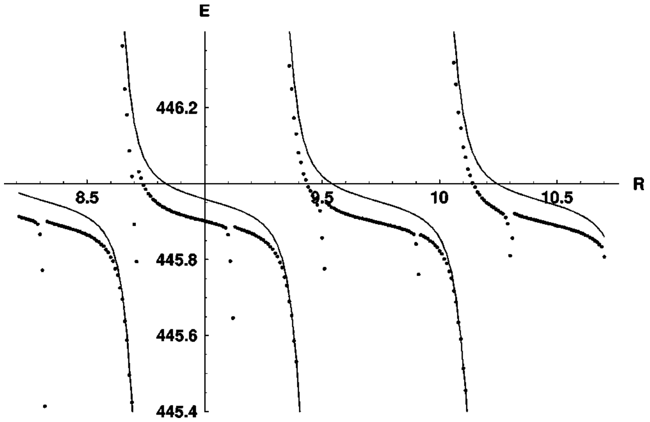

FIG. 1. The stabilization diagram for the resonance state of NaFH containing 446 cm^{-1} of energy: plot of the adiabatic energies (solid lines) and BW perturbative energies (points) obtained as functions of the distance between Na and the center of mass of the FH fragment (E in cm^{-1} and R in Å).

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