THE ADIABATIC APPROXIMATION FOR COUPLED OSCILLATORS

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The adiabatic approximation is applied to determine the quantum states of coupled oscillators described by a generalized Hénon-Heiles hamiltonian. Comparison with exact quantum and other results show that numerically calculated adiabatic energy levels are accurate even for excited states.

1. Introduction

There is considerable current interest in the properties of quantum states of systems of coupled oscillators, particularly with regard to the classical–quantum correspondence and possible manifestations of the onset of classical chaos in quantum level spectra and dynamics (see, for example refs. [1,2]). These fundamental questions have immediate relevance to theories of intramolecular energy flow and unimolecular reactions [1,2].

Semiclassical and exact quantal methods have been extensively applied to determine energy levels for coupled oscillator systems of moderate dimensionality (see, for example, refs. [3–6] and other references cited in ref. [1]). However, there remains a need for tractable, approximate quantum methods that provide computationally cheap yet reasonably accurate eigenvalues and, most importantly, *approximate quantum numbers* or constants of the motion to classify the quantum states.

The self-consistent field (SCF) approach [7,8], based on the Hartree approximation to the multimode wavefunction, is a useful method of this type. Errors inherent in the SCF approximation can in principle be corrected to arbitrary accuracy by allowing state interaction [9], and the method is suitable for systems with a large number of oscillators [10].

In this letter we describe a numerical implementation of the adiabatic approximation (AA) to calculate the quantum states of two coupled oscillators describ-ed by a generalized Hénon—Heiles (GHH) hamiltonian. The fundamental idea is to solve for motion in one coordinate, x say (taken to be the degree of freedom with highest zeroth-order frequency), at fixed values of the other coordinate y. This generates a set of adiabatic channel potentials for motion along y; the AA consists of ignoring coupling between different channels. The AA is familiar as a means of separating electronic and nuclear motions [11]. It is also central to the application of hyperspherical coordinates to describe doubly-excited states of two-electron atoms [12], collinear reaction dynamics [13–16], and bound states of molecules [17–20]. In all these cases the adiabatic channel quantum numbers are useful approximate constants of the motion for characterizing the quantum states. We find that a similar result holds for the coupled oscillator systems treated below.

A perturbative approach to the AA has recently been applied by Lin et al. [21] to calculate eigenvalues and wavefunctions for coupled oscillators. As we show below (see tables 1 and 2), energy levels obtained using perturbation theory can differ quite markedly from those obtained with a numerical approach, particularly for excited states and/or large values of the coupling constants. Our converged numerical results demonstrate the remarkable accuracy of the AA in the cases treated, even for excited states (cf. also the calculations of Christoffel and Bowman [22] on the coupled double-well oscillator).

Shapiro and Child [23] have applied the AA to

classify the exact quantum states of a modified Hénon–Heiles oscillator coupled via a doorway channel to a dissociative channel. However, their results for the Hénon–Helles system with *equal* frequencies (fig. 7 of ref. [23]) show that the AA does not accurately describe splittings of near degenerate sets of levels, as expected on general grounds.

2. Method

Consider the GHH hamiltonian

$$H = h^0(x) + h^0(y) + \lambda(yx^2 + \eta y^3) . \tag{1}$$

where h^0 is a harmonic oscillator hamiltonian in the x or y coordinate. Zeroth-order frequencies are ω_x and ω_y, with $\omega_x > \omega_y$, throughout. For fixed y, we obtain an effective x hamiltonian:

$$h(x;y) = h^0(x) + \lambda yx^2 . \tag{2}$$

Adiabatic channel functions $\Psi_\nu(x;y)$ and corresponding channel energies $\epsilon_\nu(y)$ are defined by the eigenvalue equation

$$h(x,y) \Psi_\nu(x;y) = \epsilon_\nu(y) \Psi_\nu(x;y) . \tag{3}$$

AA wavefunctions

$$\Psi_{\nu i}(x,y) = \phi_{\nu i}(y) \Psi_\nu(x,y) . \tag{4}$$

and energies $E_{\nu i}$ are then determined by solving

$$[h^0(y) + \lambda \eta y^3 + \epsilon_\nu(y)] \phi_{\nu i}(y) = E_{\nu i} \phi_{\nu i}(y) , \tag{5}$$

for each channel ν in a basis of y-oscillator functions. The HEG procedure [24] is used to integrate the channel potentials $\frac{1}{2}\omega_y^2 y^2 + \lambda \eta y^3 + \epsilon_\nu(y)$. Thus:

(i) The y-coordinate matrix is diagonalized in a basis of y-oscillator functions to generate a set of y-position eigenvalues and eigenfunctions. When $\lambda < 0$, the GHH has no true bound states, only resonances. The y-basis should not be too large in this case, otherwise spurious collapse of eigenvalues will occur in step (iii) below. A basis of 10–30 y functions is typically used, depending on the value of λ.

(ii) Eq. (3) is solved at fixed values of y equal to the eigenvalues from step (i). The resulting values of the channel energies $\epsilon_\nu(y)$ together with the transformation to the y-position representation from step (i) enable the channel potential matrices to be constructed in the original y basis. The eigenvalue eq. (3) can

be solved in two ways. First, we can use the exact result $\epsilon_\nu(y) = \hbar\omega_x(y)(\nu + \frac{1}{2})$, where the effective x frequency

$$\omega_x(y) = (\omega_x^2 + 2\lambda y)^{1/2} . \tag{6}$$

Second, the operator $h(x;y)$ can be diagonalized in a basis of 25–30 x-oscillator states with fixed frequency ω_x. n_x even only or odd only by symmetry. This latter approach allows the method to be extended to treat potentials more complicated than GHH. Both approaches give results identical to at least six significant figures for the GHH potentials studied here.

(iii) The resulting adiabatic channel matrices are diagonalized to obtain eigenvalues in the AA. The results of this numerical procedure are given in section 3.

We have also calculated the so-called diagonal non-adiabatic corrections to the channel potentials:

$$\Delta \epsilon_\nu(y) = \langle \Psi_\nu(x;y)| -\tfrac{1}{2} d^2/dy^2 |\Psi_\nu(x;y)\rangle_x . \tag{7}$$

The non-adiabatic corrections $\Delta\epsilon_\nu(y)$ were calculated both exactly, by differentiation of harmonic oscillator eigenfunctions having frequency $\omega_x(y)$, and numerically, using a three-point finite-difference method. Both approaches give identical (6–7 significant figures) results for the corrected AA eigenvalues, which are also given in section 3. The effects of interchannel non-adiabatic coupling have not been calculated.

The eigenvalue calculations described here take a small amount of CPU time on a PRIME 850 minicomputer. In numerical form, the method for determining channel eigenvalues is quite general, and can be applied to other bound state problems treated in the AA.

3. Results

Table 1 compares our results for the lowest few eigenvalues with those obtained in previous test calculations using various combinations of potential parameters. In addition to our uncorrected (AA) and diagonally corrected (CA) adiabatic energies, we give the harmonic oscillator (HO), exact quantum (EQ) [4], semi-classical (SC) [5], self-consistent field (SCF) [7] and perturbative diagonally corrected adiabatic (PCA) eigenvalues [21].

There are several points to note. As shown by Epstein [25], the uncorrected AA energy for the ground state is a *lower bound* to the true energy. By

Table 1

Comparison of eigenvalues for GHH hamiltonian: harmonic oscillator (HO); exact quantum (EQ); adiabatic approximation (AA); diagonally corrected adiabatic approximation (CA); semi-classical (SC); self-consistent field (SCF); perturbation theory diagonally corrected adiabatic (PCA). Case (A): $\omega_x^2 = 2.12581$, $\omega_y^2 = 0.29375$, $\lambda = -0.1116$, $\eta = 0.08414$; (B): $\omega_x^2 = 1.96$, $\omega_y^2 = 0.36$, $\lambda = -0.1$, $\eta = 0.1$; (C): $\omega_x^2 = 1.69$, $\omega_y^2 = 0.49$, $\lambda = -0.1$, $\eta = 0.1$; (D): $\omega_x^2 = 1.21$, $\omega_y^2 = 0.81$, $\lambda = -0.08$, $\eta = 0.1$

	n_x	n_y	HO	EQ	AA	CA	SC	SCF	PCA
(A)	0	0	1.0000	0.9916	0.9915	0.9917	0.9920	0.9925	0.9918
	0	1	1.5420	1.5159	1.5158	1.5161	1.5164	1.5190	1.5170
	0	2	2.0840	2.0308	2.0308	2.0311	2.0313	2.0364	2.0344
	1	0	2.4850	2.4188	2.4184	2.4190	2.4194	2.4214	2.4194
(B)	0	0	1.0000	0.9939	0.9938	0.9939	0.9941	–	0.9940
	0	1	1.6000	1.5809	1.5808	1.5810	1.5812	–	1.5815
	0	2	2.2000	2.1612	2.1612	2.1615	2.1615	–	2.1630
(C)	0	0	1.0000	0.9955	0.9953	0.9956	0.9955	0.9963	0.9956
	0	1	1.7000	1.6870	1.6869	1.6871	1.6870	1.6895	1.6873
	0	2	2.4000	2.3750	2.3751	2.3754	2.3750	–	2.3758
	1	0	2.3000	2.2781	2.2776	2.2783	2.2782	2.2800	2.2783
	1	1	3.0000	2.9583	2.9581	2.9589	2.9584	–	2.9593
(D)	0	0	1.0000	0.9980	0.9978	0.9980	0.9978	–	0.9980
	0	1	1.9000	1.8944	1.8944	1.8947	1.8941	–	1.8947
	0	2	2.8000	2.7899	2.7903	2.7906	2.7896	–	2.7906
	1	0	2.1000	2.0890	2.0885	2.0894	2.0890	–	2.0894

the variation theorem, the diagonally corrected adiabatic ground-state energy is an upper bound to the exact energy. Our AA and CA ground-state energies should therefore bracket the EQ value, as indeed they do. The numerical CA eigenvalues are noticeably different from the PCA results, especially for case (A) (low ω_y). The CA (and PCA) results are consistently more accurate than the SCF values. This is expected, since the adiabatic wavefunction, in which the x motion changes locally according to the value of y, is much more flexible than an SCF wavefunction, in which individual modes are defined by averages over the other degrees of freedom.

Uncorrected adiabatic channel energies $\epsilon_\nu(y) + \frac{1}{2}\omega_y^2 y^2 + \lambda\eta y^3$ for n_x even are shown in fig. 1 for case (C), $\omega_x = 1.3$, $\omega_y = 0.7$, $\lambda = -0.1$, $\eta = 0.1$. At around $y \approx 8.5$, the effective force constant in the x direction vanishes, leading to a rapid drop in the channel energies beyond that point. Well below the dissociation threshold $E \approx 11.5$ units, however, the channel energies are smoothly varying and fairly parallel, so that the AA is expected to be a useful approximation there.
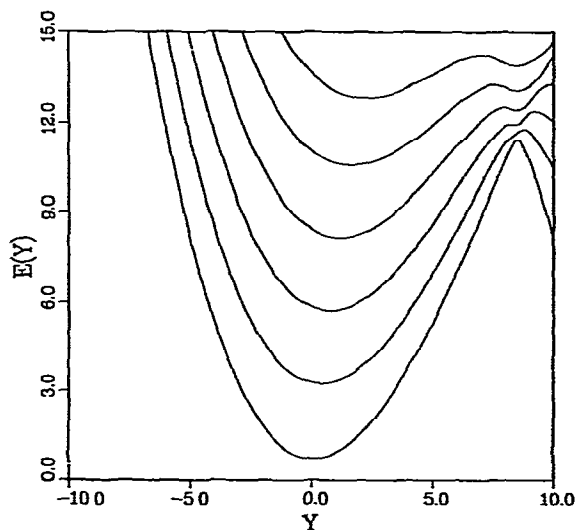

Fig. 1. Adiabatic channel energies $\epsilon(y) + \frac{1}{2}\omega_y^2 y^2 + \lambda\eta y^3$ versus y for case (C): $\omega_x^2 = 1.69$, $\omega_y^2 = 0.49$, $\lambda = -0.1$, $\eta = 0.0$. $\nu = 0, 2, 4, 6, 8, 10$ channels shown.

Table 2

Comparison of EQ, AA, CA, SC, SCF and PCA (see table 1) eigenvalues with variation in coupling constant λ. $\omega_x^2 = 1.69$, $\omega_y^2 = 0.49$, $\lambda = -\eta$

	λ	EQ	AA	CA	SC	SCF	PCA
$n_x = 0, n_y = 0$	−0.06	0.9988	0.9987	0.9988	0.9987	0.9991	0.9988
	−0.08	0.9975	0.9974	0.9975	0.9975	0.9980	0.9975
	−0.10	0.9955	0.9953	0.9956	0.9955	0.9963	0.9956
	−0.12	0.9926	0.9923	0.9927	0.9927	0.9937	0.9927
	−0.14	0.9884	0.9880	0.9885	0.9889	0.9899	0.9887
	−0.16	0.9826	0.9820	0.9827	0.9836	0.9846	0.9833
	−0.18	0.9743	0.9735	0.9745	0.9764	0.9771	0.9761
	−0.20	0.9621	0.9609	0.9631	0.9667	0.9661	0.9668
$n_x = 0, n_y = 1$	−0.06	1.6970	1.6970	1.6971	1.6970	1.6979	1.6971
	−0.08	1.6933	1.6933	1.6934	1.6933	1.6949	1.6934
	−0.10	1.6870	1.6869	1.6871	1.6870	1.6895	1.6873
	−0.12	1.6769	1.6768	1.6772	1.6770	1.6807	1.6777
	−0.14	1.6612	1.6610	1.6616	1.6617	1.6667	1.6634
	−0.16	1.6370	1.6366	1.6376	1.6382	1.6449	1.6430
	−0.18	1.5980	1.5966	1.5988	1.6010	1.6094	1.6149
$n_x = 1, n_y = 0$	−0.06	2.2932	2.2930	2.2932	2.2932	2.2936	2.2932
	−0.08	2.2870	2.2866	2.2871	2.2870	2.2881	2.2871
	−0.10	2.2781	2.2776	2.2783	2.2782	2.2800	2.2783
	−0.12	2.2658	2.2650	2.2661	2.2661	2.2688	2.2663
	−0.14	2.2490	2.2477	2.2494	2.2496	2.2536	2.2502
	−0.16	2.2257	2.2240	2.2263	2.2268	2.2327	2.2288

The results in table 2 confirm the points made above. For large coupling constants λ, the PCA energies [21] differ considerably from the CA values.

Table 3 presents a more extensive set of AA and CA eigenvalues for case (C), together with the EQ values of Noid (quoted in ref. [6]) and the SC Birkhoff normal form values of Swimm and Delos [6], for $n_x = 0$–4. The accuracy of the CA energies is quite reasonable in comparison with the SC results, especially at high energies and larger values of n_x. Apart from a reversal of the (0, 13) and (6, 2) levels, the AA unambiguously predicts the ordering of the EQ levels assigned in ref. [6]. This indicates that there is considerable regularity in the quantum spectrum for this system, even at high energies.

There is a slight upward drift of the AA and CA values relative to the EQ energies with increasing energy. Allowing for non-adiabatic interactions between channels would presumably result in a lowering of the AA and CA eigenvalues for excited states (cf. the perturbative non-adiabatic levels in ref. [21]).

4. Conclusions

Our numerical work has shown that the adiabatic approximation provides a useful description of the quantum states of two non-degenerate coupled oscillators with the GHH hamiltonian. We have taken the conventional approach and solved for the "fast" motion at fixed values of the "slow" variable. However, earlier work on a different system showed that the AA was valid over a surprisingly wide range of frequency ratios [26]. It would therefore be of interest to investigate the applicability of the present method over a similarly wide range of ratios ω_x/ω_y. The application of the AA to coupled oscillator systems with more than two dimensions also remains to be tried [20].

The AA can also be made the basis of an approximate inversion procedure [20], which, for non-degenerate systems at least, is likely to be more accurate than one based on the SC SCF method [27].

Table 3

Comparison of AA and CA eigenvalues (see table 1) with EQ values of Noid (quoted in ref. [6]) and SC values of Swimm and Delos [6] $\omega_x^2 = 1.69$, $\omega_y^2 = 0.49$, $\lambda = -0.1$, $\eta = 0.1$

n_x	n_y	EQ	AA	CA	SC	n_x	n_y	EQ	AA	CA	SC
0	0	0.9955	0.9953	0.9956	0.9955	2	0	3.5479	3.5464	3.5482	3.5480
0	1	1.6870	1.6869	1.6872	1.6870	2	1	4.2162	4.2152	4.2171	4.2164
0	2	2.3750	2.3751	2.3754	2.3750	2	2	4.8799	4.8796	4.8818	4.8803
0	3	3.0596	3.0598	3.0601	3.0595	2	3	5.5390	5.5393	5.5418	5.5397
0	4	3.7404	3.7408	3.7412	3.7404	2	4	6.1931	6.1943	6.1971	6.1944
0	5	4.4176	4.4182	4.4186	4.4176	2	5	6.8419	6.8441	6.8474	6.8443
0	6	5.0909	5.0917	5.0922	5.0910	2	6	7.4850	7.4885	7.4925	7.4891
0	7	5.7601	5.7613	5.7619	5.7605	2	7	8.1220	8.1270	8.1319	8.1288
0	8	6.4253	6.4268	6.4275	6.4260	2	8	8.7524	8.7591	8.7655	8.7632
0	9	7.0861	7.0881	7.0889	7.0873	2	9	9.3752	9.3841	9.3931	9.3921
0	10	7.7423	7.7449	7.7459	7.7445	2	10	9.9895	10.0006	10.0157	10.0152
0	11	8.3939	8.3972	8.3985	8.3973	2	11	10.5937	10.6069	10.6369	10.6326
0	12	9.0403	9.0445	9.0467	9.0456	2	12	11.1856	11.2003	11.2645	11.2439
0	13	9.6812	9.6865	9.6911	9.6894						
0	14	10.3161	10.3229	10.3331	10.3285	3	0	4.8043	4.8011	4.8045	4.8045
0	15	10.9439	10.9539	10.9754	10.9627	3	1	5.4597	5.4571	5.4610	5.4601
0	16	11.5324	11.5824	11.6203	11.5902	3	2	6.1099	6.1080	6.1124	6.1108
						3	3	6.7546	6.7536	6.7586	6.7564
1	0	2.2781	2.2776	2.2783	2.2782	3	4	7.3935	7.3934	7.3993	7.3967
1	1	2.9584	2.9581	2.9589	2.9584	3	5	8.0259	8.0270	8.0341	8.0315
1	2	3.6347	3.6349	3.6358	3.6348	3	6	8.6513	8.6539	8.6625	8.6607
1	3	4.3069	4.3076	4.3086	4.3071	3	7	9.2689	9.2731	9.2843	9.2840
1	4	4.9749	4.9762	4.9773	4.9753	3	8	9.8776	9.8836	9.8995	9.9012
1	5	5.6385	5.6405	5.6418	5.6393	3	9	10.4758	10.4834	10.5094	10.5121
1	6	6.2975	6.3002	6.3017	6.2989	3	10	11.0612	11.0688	11.1119	11.1166
1	7	6.9515	6.9552	6.9570	6.9540						
1	8	7.6003	7.6053	7.6075	7.6044	4	0	6.0463	6.0406	6.0465	6.0468
1	9	8.2435	8.2499	8.2528	8.2500	4	1	6.6878	6.6828	6.6894	6.6889
1	10	8.8805	8.8888	8.8928	8.8908	4	2	7.3234	7.3190	7.3266	7.3255
1	11	9.5108	9.5212	9.5280	9.5264	4	3	7.9524	7.9488	7.9577	7.9564
1	12	10.1332	10.1462	10.1600	10.1568	4	4	8.5743	8.5715	8.5822	8.5814
1	13	10.7463	10.7625	10.7932	10.7819	4	5	9.1882	9.1865	9.1997	9.2001
1	14	11.3484	11.3703	11.4336	11.4014	4	6	9.7932	9.7926	9.8097	9.8125
						4	7	10.3877	10.3881	10.4122	10.4183
						4	8	10.9700	10.9699	11.0092	11.0172

References

[1] D.W. Noid, M.L. Koszykowski and R.A. Marcus, Ann. Rev. Phys. Chem. 32 (1981) 267.

[2] S.A. Rice, Advan. Chem. Phys. 47 (1981) 117.

[3] K.J.S. Nordholm and S.A. Rice, J. Chem. Phys. 61 (1974) 203, 768.

[4] W. Eastes and R.A. Marcus, J. Chem. Phys. 61 (1974) 4301;
D.W. Noid and R.A. Marcus, J. Chem. Phys. 62 (1975) 2119.

[5] S. Chapman, B.C. Garret and W.H. Miller, J. Chem. Phys. 64 (1976) 502.

[6] R.T. Swimm and J.B. Delos, J. Chem. Phys. 71 (1979) 1706.

[7] J.M. Bowman, J. Chem. Phys. 68 (1978) 608.

[8] G.D. Carney, L. Sprandel and C.W. Kern, Advan. Chem. Phys. 37 (1978) 305.

[9] J.M Bowman, K. Christoffel and F. Tobin, J. Phys. Chem. 83 (1979) 905.

[10] H. Sellers, J. Mol. Struct. (Theochem) 92 (1983) 361.

[11] M. Born and J.R. Oppenheimer, Ann. Phys. 84 (1927) 457,
M. Born and K. Huang, Dynamical theory of crystal lattices (Clarendon, Oxford, 1954).

[12] U. Fano, Rept. Progr. Phys. 46 (1983) 97.

[13] A. Kupperman, J.A. Kaye and J.P. Dwyer, Chem. Phys. Letters 74 (1980) 257;
J.A. Kaye and A. Kupperman, Chem. Phys. Letters 77 (1981) 573; 78 (1981) 546; 92 (1982) 574.

[14] J. Römelt, Chem. Phys. Letters 74 (1980) 263; 87 (1982) 259;
G. Hauke, J. Manz and J. Römelt, J. Chem. Phys. 73 (1980) 5040;
J. Manz and J. Römelt, Chem. Phys. Letters 77 (1981) 172.

[15] J.M. Launey and M. Le Dournef, J. Phys. B15 (1982) L455.

[16] V. Aquilanti, S. Cavalli and A. Laganà, Chem. Phys. Letters 93 (1982) 174, 179.

[17] J. Manz, R. Meyer, E. Pollak and J. Römelt, Chem. Phys. Letters 93 (1982) 184.

[18] C.H. Greene and Ch. Jungen, in: Abstracts of Contributed Papers, XII ICPEAC, ed. S. Datz (1981) p. 1019;
C.H. Greene, Phys. Rev. A26 (1982) 2974.

[19] J. Frey and B.J. Howard, to be published.

[20] G.S. Ezra, work in progress.

[21] Q. Zhi-Ding, Z. Xing-Guo, L. Xing-Wen, H. Kono and S.H. Lin, Mol. Phys. 47 (1982) 713.

[22] K.M. Christoffel and J.M. Bowman, J. Chem. Phys. 74 (1981) 5057.

[23] M. Shapiro and M.S. Child, J. Chem. Phys. 76 (1982) 6176.

[24] D.O. Harris, G.G. Engerholm and W.D. Gwinn, J. Chem. Phys. 43 (1965) 1515.

[25] S.T. Epstein, J. Chem. Phys. 44 (1966) 836.

[26] R.S. Caswell and M. Danos, J. Math. Phys. 11 (1970) 349.

[27] R.B. Gerber, R.M. Roth and M.A. Ratner, Mol. Phys. 44 (1981) 1335.