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Adiabatic multi-step separation method and its application to coupled oscillators

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Extension of the adiabatic approach to a multi-step separation method is presented. This method step by step reduces the multi-dimensional Schrödinger equation to the effective equations of lower dimensions. The reduction procedure allows to take advantage of multi-level hierarchy of various physical systems. The multi-step separation method is applied in the calculation of vibrational energies of coupled oscillators. The new method is found to be very effective and accurate.

Key words: Adiabatic multi-step separation method — Coupled oscillators — Hierarchy — Multi-dimensional problem — Reduced wavefunctions

1. Introduction

In the description of many-body systems the approximate methods are usually applied which allow to reduce the multidimensional Schrödinger equation to the effective equations of a lower dimension. Such approximations are performed with the adiabatic Born–Oppenheimer (BO) method [1, 2] and its modification, the adiabatic Born–Huang (BH) method [3]. The BO and BH methods make use of the hierarchy within the molecule structure in which the electron motion creates the effective potential for the nuclei. Thus, the nuclei are in a way subordinated to the electrons. The essence of the adiabatic methods is a division of the whole configuration space of the system into the subspace of electron coordinates (r_e) and the subspace of nuclear coordinates (r_n). Then the hierarchy of these subspaces is fixed. The electron coordinates (r_e) are treated as "more important" so in the beginning the electron function $\tilde{\phi}_e$ and electron energy $\mathscr{E}_e$ are determined which parametrically depend on (r_n):

$$(H - T_n - \mathscr{E}_e(r_n))\tilde{\phi}_e(r_e; r_n) = 0 \tag{1}$$

where H is the total Hamiltonian of a molecule and T_n is the kinetic energy of the nuclei.

In the second step the nuclear function $\tilde{\phi}_n(r_n)$ and approximate energy of the system $\mathscr{E}$ are determined from the equation:

$$(T_n + \mathscr{E}_e(r_n) - \mathscr{E})\tilde{\phi}_n(r_n) = 0 \tag{2}$$

in which $\mathscr{E}_e(r_n)$ is treated as a potential. The approximated total wavefunction $\tilde{\phi}(r_e, r_n)$ is defined as

$$\tilde{\phi}(r_e, r_n) = \tilde{\phi}_e(r_e; r_n)\tilde{\phi}_n(r_n). \tag{3}$$

The hierarchy in the adiabatic methods determines the sequence of the separation of variables, i.e. the sequence of the determination of effective wavefunctions for the two subsystems: electrons and nuclei.

There are a lot of physical systems the structure of which reveals a complicated multi-level hierarchy. For example a molecule. Within its electron subsystem various types of states can be distinguished e.g. Rydberg states, valence states, core states (see for example the monograph of Herzberg [4]). Within its nuclear subsystem we can distinguish the states connected with low-frequency nuclear motions (inversional and torsional motions), with nuclear motions of medium frequencies (ring vibrations) and with those of high frequencies (vibrations of light atoms) [5].

In this paper we propose the multi-step adiabatic method of reducing the variables in a multi-dimensional problem. This new method provides the possibility to take advantage of the multi-level hierarchy of physical systems.

We study this method in the multi-dimensional problem of coupled oscillators (CO). The CO models represent molecular vibrations, so they are widely used in the vibrational spectroscopy of molecules [6, 7], in the theory of intramolecular energy transfer and unimolecular reactions [8, 9].

The calculations of energy levels of CO is a serious problem. Most often the variational Ritz method is applied, however its application is limited by the size of the basis growing quickly by increasing the dimension of the problem.

Recently, various approximate methods have been studied intensively as to their application to the CO problem. So far most of the works concerned semiclassical approximation [10–16], SCF [7, 17–19] and SCF CI [19–21] methods. Quite recently, an adiabatic method was also applied in the calculations of vibrational energies of molecules [22–24] as well as in the study of the model systems such as Barbanis [25], Caswell-Danos [25] and Hénon-Heiles [26, 27] CO.

In this paper we study the efficiency of the adiabatic multistep separation in the CO problem. This method reduces the multi-dimensional problem by a multi-step procedure. We prove that the method discussed is easy to be applied and is very useful in the CO problem.

2. Reduced wavefunctions and effective potentials

Let us consider a system with many degrees of freedom. Having assumed that it has a hierarchic structure let us divide the configuration space X of its variables into subspaces: $X\equiv(x_1, x_2, \dots, x_N)=(1, 2, \dots, k, \dots, n)$ where $k\equiv(x_{k_1}, x_{k_2}, \dots, x_{k_m})$ stands for the kth subspace connected with the kth subsystem.

The approximate wavefunction of the system described by the Hamiltonian

$$H=\sum_k T_k(k)+V(1,2,\dots,n) \tag{4}$$

we define in the form

$$\tilde{\phi}(1,2,\dots,n)=\tilde{\phi}_1(1;2,\dots,n)\tilde{\phi}_2(2;3,\dots,n)\cdots\tilde{\phi}_n(n) \tag{5}$$

where the functions $\tilde{\phi}_k(k;k+1,\dots,n)$ we will determine from the equations of the following general form:

$$[T_k(k)+\tilde{V}_k(k,k+1,\dots,n)-\tilde{\mathscr{E}}_k(k+1,\dots,n)]\tilde{\phi}_k(k;k+1,\dots,n)=0. \tag{6}$$

The variables $k+1,\dots n$ in the kth equation are the parameters as they do not appear in the differential operators $T_k(k)$.

In order to determine effective potentials $\tilde{V}_k$ so that they reflect the hierarchy of the system and give good approximation for its wavefunction ψ let us consider the functions $\tilde{\phi}_k$. They are connected with the reduced density matrices [28–33] which are defined by the relations:

$$\rho^{(k)}(k,\dots,n)=\langle\psi(1,2,\dots,n)|\psi(1,2,\dots,n)\rangle_{1,\dots,k-1} \tag{7}$$

where

$$\langle\psi|\psi\rangle_0\equiv|\psi|^2$$

and

$$\langle\psi|\psi\rangle_{1,\dots,n}=1 \text{ (normalization condition).}$$

It is easy to calculate $\tilde{\rho}^{(k)}$ for the approximate wavefunction of the form (5) provided that the following normalization condition is imposed on the $\tilde{\phi}_k$ functions:

$$\langle\tilde{\phi}_k(k;\dots,n)|\tilde{\phi}_k(k;\dots;n)\rangle_k=1. \tag{8}$$

This condition can always fulfilled if Eqs. (6) are linear. Then, we have:

$$\rho^{(k)}=\langle\tilde{\phi}|\tilde{\phi}\rangle_{1,2,\dots,k-1}=\prod_{l=k}^{n}|\tilde{\phi}_l(l;\dots;n)|^2 \tag{9}$$

and

$$\begin{aligned}|\tilde{\phi}_k|^2&=\tilde{\rho}^{(k)}(k,\dots,n)/\tilde{\rho}^{(k+1)}(k+1,\dots,n)\\&=\langle\tilde{\phi}(1,\dots,n)|\tilde{\phi}(1,\dots,n)\rangle_{1,\dots,k-1}/\langle\tilde{\phi}(1,\dots,n)|\tilde{\phi}(1,\dots,n)\rangle_{1,\dots,k}.\end{aligned} \tag{10}$$

As can easily be seen, the functions $\tilde{\phi}_k$ are strictly connected with $\tilde{\rho}^{(k)}$ so we will further refer to them as the reduced wavefunctions (RWF).

It is worth noticing that RWF can be calculated not only for the approximate wavefunction $\tilde{\phi}$ but for the exact ψ as well. The exact RWF ϕ_k defined by

$$|\phi_k|^2 = \rho^{(k)}(k, \ldots, n)/\rho^{(k+1)}(k+1, \ldots, n) \tag{11}$$

has the analogical properties as the approximate ones, namely they obey condition (8) which follows directly from Eq. (11) and fulfil Eq. (9).

Now, let us consider the relation between $\{\phi_k\}$ and the energy E of the system. Let us calculate the integral $\langle\psi T_k \psi\rangle_{1,\ldots,n}$. As the operator T_k

$$T_k = -(\hbar^2/2) \sum_{i \in k} m_i^{-1} \partial^2/\partial x_i^2 \tag{12}$$

does not act on the functions $\phi_{k+i}(i > 0)$, it is sufficient to calculate $\langle\phi_k \cdots \phi_1 T_k \phi_1 \cdots \phi_k\rangle_{1,\ldots,k}$.

From Eq. (8) for ϕ_k it follows:

$$\partial/\partial x_i \langle\phi_k|\phi_k\rangle_k = 2\langle\phi_k \partial/\partial x_i \phi_k\rangle_k = 0 \text{ for } i \in l = 1, \ldots, n \tag{13}$$

which implies:

$$\langle\psi T_k \psi\rangle_{1\cdots n} = \prod_{l=1}^{k} \langle|\phi_k|^2 \cdots |\phi_{l+1}|^2 \langle\phi_l T_k \phi_l\rangle_l\rangle_{l+1,\ldots,n}.$$

So, the expression for energy can now be rewritten in the recurrential form:

$$\mathscr{E}_{k+1}(k+1, \ldots, n) = \langle\phi_k|T_k + V_k^{\text{eff}}|\phi_k\rangle_k \tag{14}$$

where

$$V_k^{\text{eff}}(k, \ldots, n) = \mathscr{E}_k(k, \ldots, n) + \sum_{l=1}^{k-1} A_{k,l}(k, \ldots, n) \tag{15}$$

where

$$A_{k,l} = \langle|\phi_{k-1}|^2 \cdots |\phi_{l+1}|^2 \langle\phi_l T_k \phi_l\rangle_l\rangle_{l+1,\ldots,k-1} \tag{16}$$

and

$$\mathscr{E}_1 \equiv V(1, \ldots, n), \qquad \mathscr{E}_{n+1} \equiv E.$$

If we divide the configurational space into subspaces and arrange them in a certain way, i.e. introduce a certain hierarchy, then for each subspace which we will further identify with the kth group of particles of quasiparticles in the system, a RWF exists which depends only on the variables (k) and on less important $(k+1, \ldots, n)$. The functions $\{\phi_l\}_{l=1}^{k}$ allow to calculate $\mathscr{E}_{k+1}(k+1, \ldots, n)$ which has the meaning of the average energy of the kth group of particles, and $A_{k,l}(k, \ldots, n)$ which represent kinematic couplings of the kth group with the more important $(1, \ldots, k-1)$ groups. $A_{k,l}$ will be further referred to as kth kinematical correction of $(k-l)$th order. The V_k^{eff} represents the effective potential of the kth group of particles. The above results extend the meaning of RWF and the effective potential which has been proposed by Hunter [34-36] for the case of the division of the configurational space into two. We would like to propose an approximate method to calculate V_k^{eff} and ϕ_k.

3. Adiabatic multi-step separation method

We are interested in the problem of approximate determination of RWF ϕ_k and effective potentials V_k^{eff}. We would like to calculate them from the equations of the form (6). These equations are postulated to have their structure consistent with the structure of Eqs. (14–16). Under these conditions we obtain:

$$\left[T_k + \mathscr{E}_k^{\mathscr{A}} + \sum_{l=1}^{k-1} A_{k,l}^{\mathscr{A}} - \mathscr{E}_{k+1}^{\mathscr{A}}\right] \phi_k^{\mathscr{A}} = 0, \qquad k = 1, \ldots, n \tag{17}$$

where

$$\mathscr{E}_1^{\mathscr{A}} = V(1, 2, \ldots, n), \qquad \mathscr{E}_{n+1}^{\mathscr{A}} \equiv \mathscr{E}^{\mathscr{A}}.$$

We will now show that $\mathscr{E}^{\mathscr{A}}$, defined as above, is an upper bound of the ground-state energy E of the system. With regard to Eqs. (14–17) and assuming the functions ϕ_k^A as normalized with respect to the relevant variables (k) we obtain

$$\mathscr{E}^{\mathscr{A}} = \langle \phi^{\mathscr{A}} H \phi^{\mathscr{A}} \rangle_{1,\ldots,n} \qquad \phi^A = \prod_{k=1}^{n} \phi_k^A$$

The variational principle for the Schrödinger equation $(H - E)\psi = 0$ leads to

$$\mathscr{E}^{\mathscr{A}} = \langle \phi^{\mathscr{A}} H \phi^{\mathscr{A}} \rangle_{1,\ldots,n} \geq \langle \psi H \psi \rangle_{1,\ldots,n} = E.$$

It is worth noting that for $n = 2$ Eq. (17) defines the adiabatic BH approximation applied in the description of molecular systems. Hence, these equations represent the extension of the BH method.

At $n > 2$, the inclusion of all kinematic corrections $A_{k,l}^{\mathscr{A}}$ and especially those of higher order is beset with difficulties, however, equations of the type (17) can be postulated in which some of the corrections do not occur.

Let us denote by $\mathscr{A}$ the set of indices (k, l) labelling all the corrections $A_{k,l}^{\mathscr{A}}$ occurring in equation (17), and let $\mathscr{X}$ stand for the subset $\mathscr{X} \subset \mathscr{A}$, and $\bar{\mathscr{X}} = A \backslash \mathscr{X}$.

We assume the equations in the form:

$$\left[T_k + \mathscr{E}_k^{\mathscr{X}} + \sum_{\substack{l=1 \\ (k,l) \in \mathscr{X}}}^{k-1} A_{k,l}^{\mathscr{X}} - \mathscr{E}_{k+1}^{\mathscr{X}}\right] \phi_k^{\mathscr{X}} = 0, \qquad k = 1, \ldots, n \tag{18}$$

where the definitions of $A_{k,l}^{\mathscr{X}}$ and $\mathscr{E}_1^{\mathscr{X}}$ are analogous to those of Eq. (17), and proceed to explain how to assess the accuracy of the approximation assumed.

4. The accuracy of the extended adiabatic approximation

The accuracy of the approximate wavefunction ϕ^X and energy $\mathscr{E}^{\mathscr{X}}$ determined from Eq. (18) depends on the fact whether the division of the space as well as the hierarchy assumed correctly reflect the structure of the system. The exact energy E calculated from Eqs. (14-16) does not depend on that, because the exact RWF's $\{\phi_k\}$ include the information about the whole system since they are determined by the exact ψ of the whole system. Therefore a change in the division of the space immediately leads to the corresponding change in $\{\phi_k\}$. It is easy to note that the adiabatic RWF's $\{\phi_k^A\}$ do not have such property as each of them comprises only a piece of information about the system. The equation for the adiabatic kth RWF only takes into account the more important subsystems $l=1,\ldots,k-1$ which means that the adiabatic approximation assumes a one-direction coupling between the subsystems (the less important system is subordinated to the more important one with no feedback possible). Thus, the problem of the adequacy of the approximation assumed influencing the accuracy of the energy determination is of great importance. In the following we will give the relations allowing to estimate this accuracy for the ground-state of arbitrary system.

The following inequalities are fulfilled (the proof is given in Appendix 7.1)

$$E \leq \mathscr{E}^{\mathscr{X}} + \sum_{(k,l)\in\mathscr{X}} \langle \phi_n^{\mathscr{X}} \cdots \phi_k^{\mathscr{X}} A_{k,l}^{\mathscr{X}} \phi_k^{\mathscr{X}} \cdots \phi_n^{\mathscr{X}} \rangle_{k,\ldots,n}, \tag{19a}$$

$$\begin{aligned} E \geq \mathscr{E}^{\mathscr{X}} &+ \sum_{(k,l)\in\mathscr{X}} \langle \phi_n \cdots \phi_k | A_{k,l} - A_{k,l}^{\mathscr{X}} | \phi_k \cdots \phi_n \rangle_{k,\ldots,n} \\ &+ \sum_{(k,l)\in\bar{\mathscr{X}}} \langle \phi_n \cdots \phi_k A_{k,l} \phi_k \cdots \phi_n \rangle_{k,\ldots,n}. \end{aligned} \tag{19b}$$

The preceding inequality can serve for assessing the accuracy of extended BH method. Indeed, by putting $\mathscr{X}=\mathscr{A}$ (taking into account all the corrections $A_{k,l}^{\mathscr{A}}$), we obtain

$$\sum_{(k,l)\in\mathscr{A}} \langle \phi_n \cdots \phi_k | A_{k,l}^{\mathscr{A}} - A_{k,l} | \phi_k \cdots \phi_n \rangle_{k,\ldots,n} \geq \mathscr{E}^{\mathscr{A}} - E \geq 0. \tag{20}$$

The accuracy of BH method is, thus, given by the sum of the averaged with the $\{\phi_k\}$ differences between the exact and the adiabatic kinematical corrections which, averaged, are too large.

Assume we include no corrections $A_{kl}^{\mathscr{X}}$ in Eqs. (18) in which case $\mathscr{X}=\varnothing$. We then obtain equations analogous to those of $\mathscr{BO}$. Applying the inequalities (19a, b) we have:

$$\sum_{(k,l)\in\mathscr{A}} \langle \phi_n^{\mathscr{BO}} \cdots \phi_k^{\mathscr{BO}} A_{k,l}^{\mathscr{BO}} \phi_k^{\mathscr{BO}} \cdots \phi_n^{\mathscr{BO}} \rangle_{k,\ldots,n} \geq E - \mathscr{E}^{\mathscr{BO}} \geq 0 \tag{21}$$

signifying that the extended $\mathscr{BO}$ method gives a lower bound to the energy, as in the case of $n=2$ [37, 38].

Between $\mathscr{E}^{\mathscr{X}}$ and $\mathscr{E}^{\mathscr{BO}}$ the following relation holds:

$$\begin{aligned} &\sum_{(k,l)\in\mathscr{X}} \langle \phi_n^{\mathscr{BO}} \cdots \phi_k^{\mathscr{BO}} A_{k,l}^{\mathscr{X}} \phi_k^{\mathscr{BO}} \cdots \phi_n^{\mathscr{BO}} \rangle_{k,\ldots,n} \geq \mathscr{E}^{\mathscr{X}} - \mathscr{E}^{\mathscr{BO}} \\ &\quad \geq \sum_{(k,l)\in\mathscr{X}} \langle \phi_n^{\mathscr{X}} \cdots \phi_k^{\mathscr{X}} A_{k,l}^{\mathscr{X}} \phi_k^{\mathscr{X}} \cdots \phi_n^{\mathscr{X}} \rangle_{k,\ldots,n} \geq 0 \end{aligned} \tag{22}$$

stating that the result obtained on the rejection of an arbitrary number of corrections $A^{\mathscr{X}}_{k,l}$ is not lower than $\mathscr{E}^{\mathscr{BO}}$

In the special case of $\mathscr{X}=\mathscr{A}$ the relations (22) permit the evaluation of the difference $\mathscr{E}^{\mathscr{A}}-\mathscr{E}^{\mathscr{BO}}$ which is an estimation of maximum error given by extended $\mathscr{BO}$ or BH methods.

5. Adiabatic multi-step separation method for coupled oscillators

In this section we will show that the extended adiabatic method is very useful in calculations of eigenenergies of the multi-dimensional Schrödinger equation for COs.

We will study the accuracy of the method presented for the generalized Hénon-Heiles CO model defined by the three-dimensional Hamiltonian

$$H(x_1, x_2, x_3)=\sum_{i=1}^{3} h_i(x_i)+V_c(x_1, x_2, x_3) \tag{23}$$

with

$$h_i(x_i)=\tfrac{1}{2}(-\partial^2/\partial x_i^2+(\omega_i x_i)^2+2a_{i,0}x_i^3) \tag{24a}$$

and

$$V_c=a_{1,2}x_1x_2^2+a_{1,3}x_1^2x_3. \tag{24b}$$

Recently, the energies of this Hamiltonian have been calculated by applying semiclassical [15, 16], SCF and SCF CI [19] methods.

We will solve Eq. (17) for Hamiltonian (23) applying perturbation theory because usually $|a_{i,j}| \ll 1$ (we will take $a_{1,0}=a_{3,0}=-0.01$, $a_{2,0}=0$ and $a_{1,2}=a_{1,3}=-0.1$, the same as in Refs. [16, 19]). In calculations we will neglect all the terms lower than 10^{-4}.

Let us divide the space $X=(x_1, x_2, x_3)$ into subspaces $1=(x_1)$, $2=(x_2)$, $3=(x_3)$ and let us calculate the adiabatic energies from Eq. (17) in which we will also neglect some kinematic corrections $A_{k,l}$. The method of solving this equation is described in the Appendix. The numerical values of the energies $E^{\mathscr{BO}}(A_{k,l}=0)$, $E^{\mathscr{X}}(A_{1,2}\neq 0)$, and $E^{\mathscr{A}}(A_{k,l}\neq 0)$ for the states (n_1, n_2, n_3) are given in Table 1, and they are compared with the SCF and SCF CI energies. We see that the adiabatic method gives reasonable results although the frequencies ω_i of the oscillators are comparable. Let us note that for all states considered except the state (1, 0, 0) which strongly interacts with the state (0, 0, 2) as $\omega_1 \cong 2\omega_3$ the relations $E^{\mathscr{BO}}<E$ and $E^{\mathscr{A}}>E$ hold. These relations allow to estimate the accuracy of adiabatic energies when the exact energy E is not known because $\Delta E^{\mathscr{A}} \cong E^{\mathscr{A}}-E<E^{\mathscr{A}}-E^{\mathscr{BO}}$.

This accuracy depends on the order in which the variables are reduced i.e. on the hierarchy assumed, but for our CO model this hierarchy is not obvious. In order to prove whether the hierarchy assumed corresponds to the real hierarchy

Table 1. Adiabatic energies $E^{\mathscr{BO}}(A^{\mathscr{A}}_{k,l}=0)$, $E^{\mathscr{X}}(A^{\mathscr{X}}_{2,1}\neq 0)$ and $E^{\mathscr{A}}(A^{\mathscr{A}}_{k,l}\neq 0)$ calculated by the reducing of variables: $x_1\rightarrow x_2\rightarrow x_3$, and E^{SCF} and $E^{\mathrm{SCF\,CI}}$ energies of the three-dimensional CO. $\omega_1=1.3$, $\omega_2=1$, $\omega_3=0.7$, $a_{1,0}=a_{3,0}=-0.01$, $a_{1,2}=a_{1,3}=-0.1$

n_1	n_2	n_3	$\mathscr{BO}$	$\mathscr{X}$	$\mathscr{A}$	SCF[a]	SCF CI[a]
0	0	0	1.4926	1.4950	1.4953	1.4951	1.4938
0	0	1	2.1842	2.1868	2.1870	2.1884	2.1852
0	1	0	2.4827	2.4899	2.4901	2.4883	2.4883
1	0	0	2.7738	2.7812	2.7815	2.7782	2.7721
0	1	1	3.1739	3.1815	3.1818	3.1815	3.1770
0	0	2	2.8726	2.8752	2.8754	2.8786	2.8736

[a] Calculated in [19]

in the system, let us calculate the energies of CO reducing variables in the order $x_2\rightarrow x_1\rightarrow x_3$. The results given in Table 2 show that although the frequency of the first oscillator ω_2 is less than ω_1 this reduction is much more effective than the previous one. These results are also much better than SCF results.

In order to analyse this interesting result let us calculate adiabatic energies in both schemes of reduction for various values of the frequency ratios $\mu_{kl}\equiv\omega_k/\omega_l$. The adiabatic energies included in Table 3 show that for $\mu_{32}\lessapprox 0.5$ both schemes

Table 2. Adiabatic energies $E^{\mathscr{BO}}$, $E^{\mathscr{X}}$ and $E^{\mathscr{A}}$ calculated by the reducing of variables: $x_2\rightarrow x_1\rightarrow x_3$, and $E^{\mathrm{SCF\,CI}}$ (exact) energies of the three-dimensional CO. The parameters ω_i and $a_{k,l}$ are the same as in Table 1

n_1	n_2	n_3	$\mathscr{BO}$	$\mathscr{X}$	$\mathscr{A}$	SCF CI[a]
0	0	0	1.4932	1.4939	1.4941	1.4938
0	0	1	2.1848	2.1855	2.1857	2.1852
0	1	0	2.4843	2.4864	2.4866	2.4857
1	0	0	2.7724	2.7731	2.7738	2.7721
0	1	1	3.1757	3.1777	3.1780	3.1770
0	0	2	2.8732	2.8739	2.8741	2.8736

[a] Calculated in [19]

Table 3. Adiabatic energies $E^{\mathscr{BO}}$, $E^{\mathscr{X}}$ and $E^{\mathscr{A}}$ calculated for the ground state of CO in both reduction schemes: I $(x_1\rightarrow x_2\rightarrow x_3)$ and II $(x_2\rightarrow x_1\rightarrow x_3)$ for various μ_{kl} values. $\omega_3=0.7$, $a_{1,0}=a_{3,0}=-0.01$, $a_{1,2}=a_{1,3}=-0.1$

	μ_{32}	0.7	0.7	0.7	0.5	0.5	0.5	0.3	0.3	0.3
	μ_{21}	0.7	0.5	0.3	0.7	0.5	0.3	0.7	0.5	0.3
	$\mathscr{BO}$	1.5581	1.8464	2.5148	2.0469	2.4480	3.3821	3.1817	3.8488	5.4046
I	$\mathscr{X}$	1.5599	1.8470	2.5149	2.0473	2.4481	3.3821	3.1818	3.8488	5.4046
	$\mathscr{A}$	1.5600	1.8471	2.5149	2.0474	2.4481	3.3821	3.1818	3.8488	5.4046
	$\mathscr{BO}$	1.5585	1.8464	2.5146	2.0470	2.4480	3.3820	3.1818	3.8488	5.4046
II	$\mathscr{X}$	1.5591	1.8471	2.5153	2.0472	2.4481	3.3822	3.1818	3.8488	5.4047
	$\mathscr{A}$	1.5593	1.8471	2.5153	2.0472	2.4481	3.3822	3.1818	3.8488	5.4047

work very well ($\Delta E^{\mathcal{A}} \lesssim 10^{-4}$) and for $\mu_{21} \gtrsim 0.5$ the second scheme is more effective. So, we see, that a reduction of the variables in order of decreasing frequencies is not always the best. This fact indicates that the hierarchy in the system of CO is not solely determined by μ_{kl}.

In order to answer the question which parameters determine the hierarchy in the system of CO let us calculate the errors $\Delta E^{\mathcal{BO}} \equiv E^{\mathcal{BO}} - E$ determining E by perturbation theory. With an accuracy to $a_{k,l}^2$ for both reduction schemes we obtain

$$\Delta E^{\mathcal{BO}} = \Delta E_{1,2}^{\mathcal{BO}} + \Delta E_{1,3}^{\mathcal{BO}}, \tag{25}$$

where

$$\Delta E_{1,2}^{\mathcal{BO}}(x_1 \to x_2 \to x_3) = \omega_1 \gamma_{21}^2 (\mu_{21} M_2 - 2 N_1 N_2)(\mu_{21}(1 - 4\mu_{21}^2))^{-1}, \tag{26a}$$

$$\Delta E_{1,2}^{\mathcal{BO}}(x_2 \to x_1 \to x_3) = \omega_2 \gamma_{12}^2 (M_1 - 2\mu_{12} N_1 N_2)(4(\mu_{12}^2 - 4))^{-1}, \tag{26b}$$

$$\begin{aligned} \Delta E_{1,3}^{\mathcal{BO}}(x_1 \to x_2 \to x_3) &= \omega_1 \gamma_{31}^2 (M_1 - 2\mu_{31} N_1 N_3)(4(\mu_{31}^2 - 4))^{-1} \\ &= E_{1,3}^{\mathcal{BO}}(x_2 \to x_1 \to x_3) \end{aligned} \tag{26c}$$

where

$$\gamma_{kl} = a_{k,l} \omega_k^{-5/2} \tag{27}$$

and

$$N_i = n_i + 1/2; \qquad M_i = n_i^2 + n_i + 1. \tag{28}$$

We see that

1) the errors $\Delta E^{\mathcal{BO}}$ almost never depend on the anharmonicity of CO because in Eqs. (26a-26c) the terms proportional to $a_{i,0} a_{k,l}$ and $a_{i,0}^2$ do not occur.
2) the parameters determining $\Delta E^{\mathcal{BO}}$ are μ_{kl} and effective coupling constants γ_{kl} as well.
3) $|\Delta E^{\mathcal{BO}}(x_1 \to x_2 \to x_3)| > |\Delta E^{\mathcal{BO}}(x_2 \to x_1 \to x_3)|$ for $\mu_{21} \gtrsim 0.5$ for the ground state which elucidate the results in Table 3. So, for comparable frequencies $\omega_1 \cong \omega_2$ the second scheme is better.

Now, let us analyse the role of kinematic corrections $A_{k,l}^{\mathcal{A}}$ (we will consider here the first reduction scheme). If $A_{2,1}^{\mathcal{A}}$ is taken into account, then for $\mu_{21} \ll 1$, $\Delta E_{1,2}^{\mathcal{X}} \cong \omega_1 \gamma_{21}^2 M_2$ and if $A_{3,1}^{\mathcal{A}}$ is taken into account, then $\Delta E_{1,3}^{\mathcal{A}} \cong \omega_1 \gamma_{31}^2 \mu_{31} N_1 N_2/8$. So, these corrections improve the adiabatic energies. They are essential for the strong couplings between the oscillators.

6. Conclusions

We proposed a new method for the solution of multi-dimensional problems. The main idea of this method is a division of the whole configurational space of the physical system into subspaces according to the hierarchy in the system. This hierarchy determines the sequence of reduction of dynamical variables describing the subsystems. This reduction allows to calculate the reduced wavefunctions and effective potentials for each subsystem and in consequence the total wavefunction and energy of the system considered. Thus, the adiabatic multi-step separation method is very convenient for treating multi-level hierarchical systems.

We have applied this method to solve the multi-dimensional CO problem. We have found the parameters determining the hierarchy in the CO system. They are not only μ_{kl} but also the effective coupling constants γ_{kl}. Thus the adiabatic method gives very good results even for $\mu_{kl}=1$ because, usually, $|\gamma_{kl}| \ll 1$ as in the CO model considered.

The accuracy of the adiabatic energies hardly depends on the anharmonicity of CO, so this method can be used for a wide class of anharmonic CO.

Adiabatic equations for CO can be solved rather simply without iterations as in SCF method. Simplicity and accuracy of the method proposed make them very useful in the CP problem.

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7. Appendix

7.1. Estimations of the adiabatic energy errors

Here we derive the relations (19a, b). From the variational principle for the Schrödinger equation we have

$$E = \langle \psi H \psi \rangle_{1,\ldots,n} \leq \langle \phi^{\mathscr{X}} H \phi^{\mathscr{X}} \rangle_{1,\ldots,n} \equiv \bar{\mathscr{E}}^{\mathscr{X}} \tag{29}$$

where $\bar{\mathscr{E}}^{\mathscr{X}} \equiv \bar{\mathscr{E}}^{\mathscr{X}}_{n+1}$ is calculated from Eqs. (14–16) in which ϕ_k should be replaced by ϕ_k^X, i.e.

$$\bar{\mathscr{E}}^{\mathscr{X}}_{k+1} = \langle \phi^{\mathscr{X}}_k | T_k + \bar{\mathscr{E}}^{\mathscr{X}}_k + \sum_{\substack{l \\ (k,l)\in\mathscr{A}}} A^{\mathscr{X}}_{k,l} | \phi^{\mathscr{X}}_k \rangle_k.$$

Let us take the first equation from Eq. (18) with the index K in which some kinematic corrections $A^{\mathscr{X}}_{K,l}$ do not occur. Then we have $\bar{\mathscr{E}}^{\mathscr{X}}_K = \mathscr{E}^{\mathscr{X}}_K$ and

$$\begin{aligned} \bar{\mathscr{E}}^{\mathscr{X}}_{K+1} &= \langle \phi^{\mathscr{X}}_K | T_K + \mathscr{E}^{\mathscr{X}}_K + \sum_{\substack{l \\ (K,l)\in\mathscr{X}}} A^{\mathscr{X}}_{k,l} + \sum_{\substack{l \\ (K,l)\in\bar{\mathscr{X}}}} | A^{\mathscr{X}}_K \rangle_K \\ &= \mathscr{E}^{\mathscr{X}}_{K+1} + \sum_{\substack{l \\ (K,l)\in\bar{\mathscr{X}}}} \langle \phi^{\mathscr{X}}_K A^{\mathscr{X}}_{K,l} \phi^{\mathscr{X}}_K \rangle_k. \end{aligned} \tag{30}$$

Taking this equality into account we further obtain

$$\begin{aligned} \bar{\mathscr{E}}^{\mathscr{X}}_{K+2} = \mathscr{E}^{\mathscr{X}}_{K+2} &+ \sum_{\substack{l \\ (K+1,l)\in\bar{\mathscr{X}}}} \langle \phi^{\mathscr{X}}_{K+1} A^{\mathscr{X}}_{K+1} \phi^{\mathscr{X}}_{K+1} \rangle_{K+1} \\ &+ \sum_{\substack{l \\ (K,l)\in\bar{\mathscr{X}}}} \langle \phi^{\mathscr{X}}_{K+1} \phi^{\mathscr{X}}_K A^{\mathscr{X}}_{K,l} \phi^{\mathscr{X}}_K \phi^{\mathscr{X}}_{K+1} \rangle_{K,K+1}. \end{aligned} \tag{31}$$

It is easy to see that for $K+i=n+1$ we will obtain

$$\bar{\mathcal{E}}_{n+1}^{\mathcal{X}}=\mathcal{E}^{\mathcal{X}}+\sum_{(k,l)\in\bar{\mathcal{X}}}\langle\phi_n^{\mathcal{X}}\cdots\phi_k^{\mathcal{X}}A_{k,l}\phi_k^{\mathcal{X}}\cdots\phi_n^{\mathcal{X}}\rangle_{k,\ldots,n} \tag{32}$$

which after including the relation (29) provides the inequality (19a).

We shall now prove the inequality (19b). In this order let us consider Eqs. (14) for $k<K$. By applying the variational principle to Eq. (18, $k=1$) we obtain

$$\mathcal{E}_2=\langle\phi_1|T_1+V|\phi_1\rangle_1\geq\langle\phi_1^{\mathcal{X}}|T_1+V|\phi_1^{\mathcal{X}}\rangle_1=\mathcal{E}_2^{\mathcal{X}}. \tag{33}$$

For $k=2$ we have

$$\mathcal{E}_3=\langle\phi_2|T_2+\mathcal{E}_2+A_{2,1}|\phi_2\rangle_2=\langle\phi_2|T_2+\mathcal{E}_2+A_{2,1}^{\mathcal{X}}|\phi_2\rangle_2+\langle\phi_2|A_{2,1}-A_{2,1}^{\mathcal{X}}|\phi_2\rangle_2.$$

Taking into account (33) and the variational principle for Eq. (18, $k=2$) we can write

$$\begin{aligned}\langle\phi_2|T_2+\mathcal{E}_2+A_{2,1}^{\mathcal{X}}|\phi_2\rangle_2&\geq\langle\phi_2|T_2+\mathcal{E}_2^{\mathcal{X}}+A_{2,1}^{\mathcal{X}}|\phi_2\rangle_2\\&\geq\langle\phi_2^{\mathcal{X}}|T_2+\mathcal{E}_2^{\mathcal{X}}+A_{2,1}^{\mathcal{X}}|\phi_2^{\mathcal{X}}\rangle_2=\mathcal{E}_3^{\mathcal{X}},\end{aligned}$$

thus

$$\mathcal{E}_3\geq\mathcal{E}_3^{\mathcal{X}}+\langle\phi_2|A_{2,1}-A_{2,1}^{\mathcal{X}}|\phi_2\rangle_2.$$

In a similar way we will obtain for $k=K-1$

$$\mathcal{E}_K\geq\mathcal{E}_K^{\mathcal{X}}+\sum_{(k,l)\in\mathcal{X}}\langle\phi_{K-1}\cdots\phi_k|A_{k,l}-A_{k,l}^{\mathcal{X}}|\phi_k\cdots\phi_{K-1}\rangle_{k,\ldots,K-1}.$$

Now, taking $k=K$ we have

$$\begin{aligned}\mathcal{E}_{K+1}&=\langle\phi_K|T_K+\mathcal{E}_K+\sum_{(K,l)\in\mathcal{A}}A_{K,l}|\phi_K\rangle_K\geq\langle\phi_K|T_K+\mathcal{E}_K^{\mathcal{X}}+\sum_{\substack{l\\(K,l)\in\mathcal{X}}}A_{K,l}^{\mathcal{X}}|\phi_K\rangle_K\\&\quad+\sum_{(k,l)\in\mathcal{X}}\langle\phi_K\cdots\phi_k|A_{k,l}-A_{k,l}^{\mathcal{X}}|\phi_k\cdots\phi_K\rangle_{k,\ldots,K}+\sum_{(K,l)\in\bar{\mathcal{X}}}\langle\phi_K A_{K,l}\phi_K\rangle_K.\end{aligned}$$

If we consider corresponding relations for $k=K+3,\ldots,n+1$, we will obtain inequality (19b).

In a similar way we obtain the remaining relations given in Sect. 5.

7.2. Solution of adiabatic equations

Here we solve Eqs. (17). We first consider the case when $A_{k,l}^{\mathcal{A}}=0$. The first equation $k=1$ can be written in the form

$$[-\tfrac{1}{2}\partial^2/\partial x_1^2+V_1(x_1;x_2,x_3)+V_2^o(x_2,x_3)-\mathcal{E}_2^{\mathcal{BO}}(x_2,x_3)]\phi_1^{\mathcal{BO}}(x_1;x_2,x_3)=0 \tag{34}$$

where

$$\begin{aligned}V_1&=\tilde{\omega}_1^2(x_1^2+2K_{1,2}x_1x_2^2+2K_{1,0}x_1^3)/2,\\\tilde{\omega}_1&=(\omega_1^2+2a_{1,3}x_3)^{1/2},\\V_2^o&=(\omega_2^2x_2^2+\omega_3^2x_3^2+2a_{3,0}x_3^3)/2,\\K_{i,j}&=a_{i,j}/\tilde{\omega}_1^2.\end{aligned} \tag{35}$$

Introducing the variable $x = x_1 - x_1^o$ where x_1^o is the equilibrium coordinate for which $(\partial V_1/\partial x_1)_{x_1^o} = 0$ we can write

$$[\tfrac{1}{2}(-\partial^2/\partial x^2 + (\omega x)^2) + a_{1,3}x^3 + V_1(x_1^o) + V_2^o - \mathscr{E}_2^{\mathscr{BO}}]\phi_1^{\mathscr{BO}} = 0 \tag{36}$$

where

$$\begin{aligned} x_1^o &= -K_{1,2}x_2^2(1 + 3K_{1,0}K_{1,2}x_2^2), \\ \omega^2 &= \tilde{\omega}_1^2(1 + 6K_1x_1^o), \\ V_1(x_1^o) &= -(\tilde{\omega}_1 K_{1,2}x_2^2)^2/2. \end{aligned} \tag{37}$$

Applying the perturbation theory to Eq. (36) and expanding ω^n in a power series of the variable x_2 we obtain

$$\mathscr{E}_2^{\mathscr{BO}} = \tfrac{1}{2}(w_2x_2)^2 + v_2x_2^4 + U + V_2^o \tag{38}$$

where

$$\begin{aligned} w_2 &= (\omega_2^2 - 6\tilde{\omega}_1 K_{1,0}K_{1,2}N_1)^{1/2}, \\ v_2 &= -\tilde{\omega}_1^2 K_{1,2}^2/2, \\ U &= \tilde{\omega}_1 N_1 + K_{1,0}^2 e_3(1); \end{aligned} \tag{39}$$

here

$$e_3(i) = -(7 + 60N_i^2)/16$$

and further

$$\begin{aligned} e_2(i) &= 3(1 + 4N_i^2)/8, \\ e_4(i) &= -(67 + 68N_i^2)N_i/16. \end{aligned}$$

In analogous way we solve Eq. (17, $k = 2$) with $A_{2,1}^{\mathscr{A}} = 0$ and obtain

$$\mathscr{E}_3^{\mathscr{BO}}(x_3) = \sum_{n=0}^{3} C_n x_3^n \tag{40}$$

where

$$\begin{aligned} C_0 &= \omega_1 N_1 + \omega_2 N_2(1 - d/2) + k_{1,0}^2 e_3(1) - Q(1 + d)/2 + P/4, \\ C_1 &= k_{1,3}(\omega_1 N_1 + 3d\omega_2 N_2/2 + Q(1 + 3d/2) - P), \\ C_2 &= (\omega_3^2/2) - k_{1,3}^2(2\omega_1 N_1 + 15d\omega_2 N_2 + 8Q)/4, \\ C_3 &= a_{3,0} + k_{1,3}^3\omega_1 N_1/2 \end{aligned} \tag{41}$$

where

$$\begin{aligned} k_{i,j} &= a_{i,j}\omega_1^{-2}, \\ d &= 6k_{1,0}k_{1,2}\omega_1 N_1\omega_2^{-2}, \\ Q &= e_2(2)(\omega_1 k_{1,2}/\omega_2)^2, \\ P &= e_4(2)(\omega_1 k_{1,2}/\omega_2)^4/\omega_2. \end{aligned} \tag{42}$$

Now, we find the $E^{\mathscr{BO}}$ energies as

$$E^{\mathscr{BO}} = \mathscr{E}_3^{\mathscr{BO}}(x_3^o) + \tilde{\omega}_3 N_3 + C_3^2 e_3(3)/\tilde{\omega}_3^4 \tag{43}$$

where

$$\begin{aligned} x_3^o &= ((4C_2^2 - 12C_1C_3)^{1/2} - 2C_2)/6C_3, \\ \tilde{\omega}_3 &= (2C_2 + 6C_3x_3^o)^{1/2}. \end{aligned} \tag{44}$$

In order to calculate E^A energies we determine $A_{k,l}^{\mathscr{A}}(A_{k,l}^{\mathscr{A}} \cong A_{k,l}^{\mathscr{X}} \cong A_{k,l}^{\mathscr{BO}})$

$$\begin{aligned} A_{2,1}^{\mathscr{A}} &= 2K_{1,2}^2\tilde{\omega}_1 N_1 x_2^2 + 18K_{1,2}^3 K_{1,0}\tilde{\omega}_1 N_1 x_2^4, \\ A_{3,1}^{\mathscr{A}} &= M_1 k_{1,3}^2(1 - 4k_{1,3}x_3 + 24k_{1,2}k_{1,0}N_2/\omega_2^2)/16 \\ A_{3,2}^{\mathscr{A}} &= 9M_2(k_{1,3}b)^2/64 \cong 10^{-7} \end{aligned} \tag{45}$$

where

$$b = 2\omega_1 N_1 k_{1,2}(3k_{1,0} - 2k_{1,2})/\omega_2^2. \tag{46}$$

If we take into account the correction $A_{2,1}^{\mathscr{A}}$ in Eq. (17, $k=1$) then we calculate energies denoted by $E^{\mathscr{X}}$ replacing in formulae (41) d by b. If we also take into account the correction $A_{3,1}^{\mathscr{A}}(A_{3,2}^{\mathscr{A}} \cong 0)$ then we must calculate energies denoted by $E^{\mathscr{A}}$ taking

$$C_0 + M_1 k_{1,3}^2(1 + 24k_{1,2}k_{1,0}N_2/\omega_2^2)/16$$

instead of C_0 and

$$C_1 - M_1 k_{1,3}^3/4$$

instead of C_1.

In a similar way we can calculate energies $E^{\mathscr{BO}}$, $E^{\mathscr{X}}$ and $E^{\mathscr{A}}$ for the division of the space $X = (x_1, x_2, x_3)$ into subspaces $1 = (x_2)$, $2 = (x_1)$, $3 = (x_3)$.

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