

Exotic states of diatomic molecules and methods of their description

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Various methods for representation of electronic states in diatomic molecules basing on experimental spectroscopic data are critically compared. The technique of pointwise inverted perturbation approach (IPA) is indicated as the most suitable in case of states characterized by potential energy curves substantially different from the Morse potential. Recent developments of this technique are presented.

Keywords: diatomic molecules, potential energy curves, inverted perturbation approach, molecular spectra.

1. Introduction

Our understanding of the energy structure of diatomic molecules is based on the Born–Oppenheimer approximation which takes advantage of the large disparity between the electron and nuclear masses in order to separate the electronic and nuclear coordinates. The motion of heavy nuclei can be assumed as slow compared with that of light and consequently very mobile electrons. The electronic wave functions adjust instantaneously to the positions of the nuclei and determine the potential well in which the nuclei vibrate. For separate electronic configurations diabatic potential energy curves governing the motion of the nuclei are thus obtained. However, the diabatic curves can intersect whenever potential energies associated with two different electronic configurations become equal for a given internuclear distance. Depending on the strength of the coupling between the two electronic configurations, the molecule passing through the crossing region may either remain in the original electronic state or jump to the other configuration. In the latter case the coupling can be taken into account by constructing the adiabatic potential energy curves, which change from one electronic configuration to the other along the crossing. The shape

of the adiabatic potential curves is governed by the famous non-crossing rule formulated by VON NEUMANN and WIGNER [1, 2] which forbids crossing of curves for states of the same electronic symmetry.

2. Methodology

Both the diabatic and adiabatic representations can be introduced by more rigorous definition of their properties. In the adiabatic picture the potential matrix is diagonal whereas the operator of kinetic energy of the nuclei provides the coupling terms. In the diabatic representation the potential matrix has off-diagonal elements which couple different electronic configurations and the nuclear kinetic energy operator is diagonal. It should be noted that vibrational eigenstates of neither the diabatic nor the adiabatic potential curves exactly represent the “true” (that is observed) levels, as each representation neglects some interaction matrix elements. Both representations are physically equivalent but in a given problem one may be preferable to the other. To choose an approach convenient for a specific case, Dressler introduced the so called adiabacity parameter [3]:

$$\gamma = \frac{H_{el}}{\hbar \omega_{ad}} \quad (1)$$

where the electronic matrix element coupling the diabatic states H_{el} is compared with the vibrational constant ω_{ad} of the higher-energy member of the pair of the resulting adiabatic states. If $\gamma \gg 1$ (a strongly avoided curve crossing), the vibrations of nuclei are well described in the adiabatic model and the nonadiabatic corrections to the levels are relatively small. If $\gamma \ll 1$ (a weakly avoided curve crossing), the adiabatic description fails and nuclei prefer to follow the diabatic potential curves. In the intermediate case $\gamma \approx 1$ there is a large vibronic mixing regardless of whether the diabatic or adiabatic representation is chosen.

“Exotic” states of diatomic molecules are those characterized by (adiabatic) potential energy curves whose shape is substantially different from the Morse potential. Such states originate usually from interaction between the most common valence states of a molecule with ion-pair states. At large interatomic distances the diabatic valence states display a weak R dependence (usually with the R^{-6} term as a leading one) resulting in relatively shallow potential wells. In the ion-pair states the Coulombic interaction leads to much steeper potentials (behaving as R^{-1}) and therefore diabatic curves of both types cross frequently. However, when switching to the adiabatic description, the non-crossing rule results in serious distortions of potential shapes and may lead to adiabatic potentials with barriers towards dissociation, unusual bends or shelves as well as double or even multiple minima. Such a behaviour is exemplified in Fig. 1 on selected adiabatic potential energy curves calculated for the NaK molecule [4]. For the sake of completeness it must be noted that potential

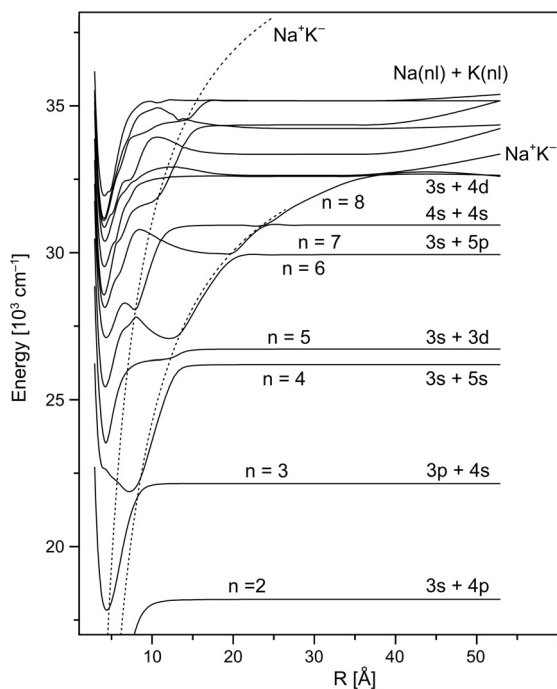


Fig. 1. Theoretical adiabatic potential energy curves for selected $n^1\Sigma_u^+$ states in NaK molecule (solid curves) [4]. Dashed curves represent diabatic potentials corresponding to the two lowest $^1\Sigma_u^+$ ion-pair states.

barriers may arise also in well separated states due to an interplay of long-range electronic and exchange forces [5].

For description of regular electronic states with Morse-like potentials it has been customary to express the energies of rovibronic levels by molecular constants as:

$$E(\nu, J) = T_e + \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + B_e [J(J+1) - A^2] - D_e [J(J+1) - A^2]^2 - \alpha_e \left(\nu + \frac{1}{2} \right) [J(J+1) - A^2] + \dots \quad (2)$$

where A stands for the quantum number of the electronic angular momentum about the internuclear axis. The same expansion can be written in a more compact form as a Dunham series:

$$E(\nu, J) = \sum_{j,k=0}^n Y_{jk} \left(\nu + \frac{1}{2} \right)^j [J(J+1) - A^2]^k \quad (3)$$

The molecular constants T_e , ω_e , $\omega_e x_e$, ... or Dunham coefficients Y_{jk} are determined by a fit to the set of measured energies of rovibrational levels. (Note that although the Dunham coefficients with $k > 1$ are not independent variables [6], in most applications all the coefficients in (3) are treated as independent parameters.) The number of parameters used depends on the accuracy of measurements. This may be illustrated by a recent study of the ground state of Rb₂ molecule, represented by as much as 62 constants [7], most of them of little physical significance. However, the required number of coefficients depends even more on the actual shape of the potential and becomes unacceptably large for potentials much different from the Morse potential. In addition, this method of description is not feasible for exotic molecular states, *e.g.*, with double-well potentials.

A more direct and physically sounder way of reducing spectroscopic data is based on representation of the investigated molecular state directly by its potential energy curve $V(R)$. Such a curve can be determined conveniently by the Rydberg–Klein–Rees (RKR) technique [8], based on the semiclassical first-order Wentzel–Kramers–Brillouin method. One of the main advantages of this technique is that no special assumptions about the mathematical form of the potential are made. Instead, the experimentally known energy levels are used to calculate points on the potential curve corresponding to the classical turning points of the nuclear motion. These points determine the potential energy curve up to the highest observed vibrational energy level.

Although widely used, the RKR method has some well-known drawbacks. First, as a semiclassical procedure it cannot provide highly precise results for systems with small reduced masses such as light hydrides [9]. Further, it is known to produce accurate potential energy curves for lower parts of potential wells but numerical instabilities and errors tend to appear for levels near dissociation limits [10]. Finally, the RKR algorithm is incapable of dealing with potentials providing more than two classical turning points (*e.g.*, double minimum potentials). For such cases fully quantum-mechanical procedures are preferable. In the analytical approach, some functional dependence $U(R)$ of the potential is assumed including a number of adjustable parameters. The energies of rovibrational levels in the given electronic state are calculated then by solving the radial Schrödinger equation with $U(R)$. The parameters are subsequently optimized to generate energy levels matching the experimental term energies. A large number of model potentials, majority of them derived from the Morse function, were proposed in the past [11, 12] but they were not sufficiently flexible to represent a real interaction potential with high accuracy except over a fairly narrow region of R . Recent years have brought considerable progress in this approach, notably the potential of SAMUELIS *et al.* [13]

$$U(R) = \sum_{i=0}^n a_i \left(\frac{R - R_m}{R + bR_m} \right)^i \quad (4)$$

or the modified Lennard–Jones potential by SETO *et al.* [7]:

$$U(R) = D_e \left[1 - \left(\frac{R_e}{R} \right)^n \exp(-\beta(z)z) \right]^2 \quad (5)$$

where $\beta(z)$ is a polynomial in $z = (R - R_e)/(R + R_e)$. These expressions have been applied successfully for potentials with regular shapes achieving high accuracy with a few fitting parameters. Until now, however, no reasonable analytical function was proposed to represent potentials with double wells or shelf regions.

A different philosophy has been adopted by KOSMAN and HINZE [14] in their inverted perturbation approach (IPA). They noticed that if the sought potential $U(R)$ is represented as an initial trial potential $U_0(R)$ plus a perturbation $\delta U(R)$, then δU can be obtained from an expression for first-order energy correction well known in perturbation theory but used in an inverse manner, namely to find an unknown perturbation from known energy corrections. In the original realization of the IPA method, the correction $\delta U(R)$ was expressed as a linear combination of some orthonormal functions $f_i(R)$ (*e.g.*, the Legendre polynomials with an exponential cutoff [15]):

$$\delta U(R) = \sum_i c_i f_i(R) \quad (6)$$

whereas an RKR potential was chosen as the initial guess. The coefficients c_i were found then by minimizing $\sum_{\nu J} |E_{\nu J}^{\text{exp}} - (E_{\nu J}^0 + \delta E_{\nu J})|$, where $E_{\nu J}^0$ is the eigenenergy calculated with $U_0(R)$ and $\delta E_{\nu J}$ denotes the energy correction associated with $\delta U(R)$, obtained within the first-order perturbation theory. The problem was thus reduced to solving an overdetermined system of linear equations for c_i (since usually one has more experimental term values to fit than c_i coefficients needed for adjusting the potential energy curve) which can be done in the least squares approximation sense. However, once $\delta U(R)$ is found it is rather ambiguous how to add the analytical correction to the initial pointwise RKR potential. Moreover, it turned out that often the correction cannot be well described by Legendre polynomials or, in fact, by any expansion of the type (6), as it would require summation of unacceptably large number of terms [16].

This limitation seriously narrowed the usefulness of the IPA method, because there was a particular need for employing it in cases of exotic potentials. Therefore recently we have proposed a modification of this procedure [17], in which the corrections to the approximate potential as well as the potential energy curve itself are defined as sets of points connected with the cubic spline function. Thus, we represent the molecular potential by a set of M grid points $\{R_k, U_k\}$ and the values U_k are fitting parameters.

We have shown that in this case the potential itself and the correction δU can be expressed as linear combinations of known functions $S_k(R)$ [17, 18] with coefficients being the corrections to the potential at the grid points:

$$U(R) = \sum_{k=1}^M S_k(R)U(R_k) \quad (7)$$

$$\delta U(R) = \sum_{k=1}^M S_k(R)\delta U(R_k) \quad (8)$$

Moreover, the formulae for the corrected eigenenergies $E_{\nu J}$ become

$$E_{\nu J} = E_{\nu J}^0 + \sum_{k=1}^M \langle \Psi_{\nu J}^0 | S_k(R) | \Psi_{\nu J}^0 \rangle \delta U(R_k) \quad (9)$$

Replacing here $E_{\nu J}$ with $E_{\nu J}^{\text{exp}}$ provides a set of N linear equations (N denotes the number of experimentally observed levels $\{\nu, J\}$) with M unknowns (where M is the number of fitted parameters, $M < N$), which should be solved in the least squares approximation sense. The proposed form for function $U(R)$ and its correction $\delta U(R)$ is very flexible and allow to represent a variety of potential energy functions, including the exotic ones. In comparison with the analytical representation the additional advantage is the relatively low degree of correlation between the fitting parameters, which leads to faster convergence of the fitting routine. A fast convergence results also from the fact that it is relatively easy to provide a good initial guess for the fitting parameters. The initial U_k can be taken from RKR or *ab initio* potentials where the uncertainties usually range from a few percent to a few tens percents. In contrast to this, the values of the coefficients used in analytic representations of potential curves are highly correlated and can vary significantly from one iteration to another or when changing the total number of fitting parameters. Besides, the low degree of correlation for the pointwise representation permits direct analysis of the reliability of the determined potential curve since the solution of the system (9) provides standard errors of the corrections δU and consequently of the generated potential curve at the grid points R_k .

Since the system of Eq. (9) is usually ill-conditioned, as an effective way for its solution the singular value decomposition (SVD) technique [19] has been chosen. Within this method the overdetermined system (9) is solved by minimizing the merit function χ^2 with a constraint that parameters on which the fit depends only weakly are not adjusted. As in our case the fitting parameters are the values of the corrections to the potential, the set of poorly determined parameters may be interpreted as regions of the potential energy curve which are insufficiently characterized by the experimental data. In effect, the SVD method ensures that the corrections are made to the potential

energy curve only in the energy range covered by the data, whereas the other parts of it remain nearly unchanged.

The procedure discussed above and nicknamed “the pointwise IPA” has been put into effect in a package of computer programs which are now commonly available [17] and were applied by us to thorough studies of electronic states in alkali dimer molecules. On the experimental side, we investigate excited electronic states accessible in one photon transitions from the ground states of homo- and heteronuclear alkali dimers, using the polarization labelling spectroscopy method [20]. This technique surmounts elegantly the difficulty of resolving and analysing highly congested molecular spectra. With a proper choice of frequencies and polarization of two independent laser beams, interacting with a given molecular sample, only transitions from a few known rovibrational levels in the ground state are observed, resulting in spectra with easily resolved and understandable rotational structure. Several of the electronic states studied by us have been characterized by exotic potentials. In most cases the adiabaticity parameters for these states were substantially greater than one thus allowing their adiabatic description, at least to a good approximation. The double minimum $2^1\Sigma_u^+$ state in Na_2 ($\gamma \approx 29$) [21] and its analogues in K_2 ($\gamma \approx 12$) [22] and Li_2 ($\gamma \approx 3$) [23] may serve as illustrative examples (Fig. 2). For all three states the potential curves constructed basing on the IPA method reproduce energies of the observed rovibrational levels with an accuracy comparable to the experimental precision (dimensionless standard errors σ of 0.7, 1.0 and 3.0, respectively). We believe that growing differences between the observed energy levels and those calculated from the constructed potential energy curves are not due to deficiencies of the IPA algorithm but rather they reflect the increasing inadequacy of

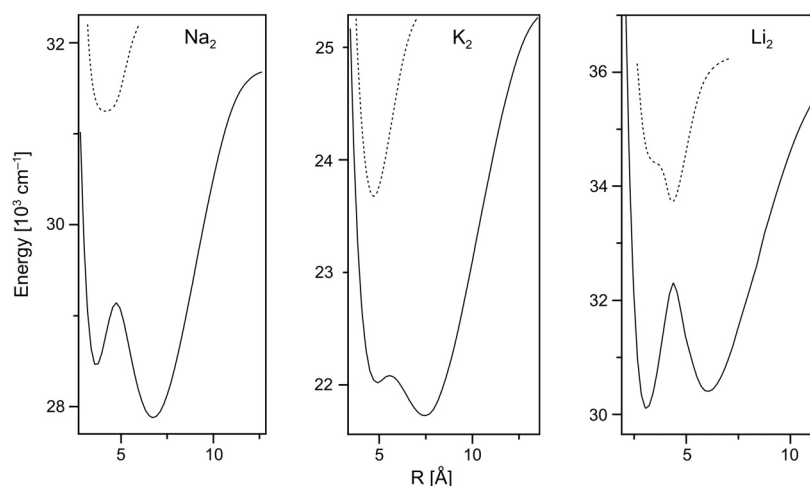


Fig. 2. The experimentally determined potential energy curves of the $2^1\Sigma_u^+$ states in Na_2 [21], K_2 [22] and Li_2 [23] molecules (solid lines) and their companion $3^1\Sigma_u^+$ states (dashed lines) resulting from avoided crossing of diabatic potential curves.

the adiabatic model when γ approaches unity. A similar problem has been encountered for the double minimum $6^1\Sigma^+$ state in NaK ($\gamma \approx 2.1$) [24] or, even to a larger extent, for strongly coupled $3^1\Pi$ and $4^1\Pi$ states in KLi [25]. In the latter case the quantum mechanical energy eigenvalues of the generated IPA potential reproduce the experimental energy levels with an accuracy 3–6 times lower than the experimental uncertainty. In this context a question may be raised whether the adiabatic potential curves are still physically meaningful in cases of strong interaction between states, like here between the $3^1\Pi$ and $4^1\Pi$. Under such circumstances our approach is purely utilitarian: we work within the adiabatic approximation as long as the generated potential curves reproduce the positions of the (great majority of) of rovibrational levels in a given state with accuracy sufficient to be helpful in assignment of the observed spectra. Fortunately, in some cases the existing experimental data allow for a global description of the mutually interacting states, as in the case of the $B^1\Pi$ and $C^1\Sigma^+$ states of KLi molecule [26]. Here the states were successfully described ($\sigma = 1.0$) in a model including two IPA potential curves of the unperturbed states plus a few constants which parameterize the coupling terms. The energy levels were obtained then by diagonalization of the matrix of the model Hamiltonian taking interaction of both states into account. Other examples of successful application of the pointwise IPA algorithm, which we would like to mention here, is our study of the $F^1\Sigma_g^+$ “shelf” state in Li_2 , where the IPA procedure has proved the existence of a shallow second minimum in the molecular potential, unobservable by spectroscopic methods [27], and construction of potential curve for the $D^1\Pi$ state in KLi with a potential barrier to dissociation, based on observation of all vibrational levels supported by the potential well [28].

The examples listed above indicate that the pointwise IPA method, being model-free, imposes principally no limitation on the shape of the fitted potential energy curve. But the pointwise approach has also disadvantages following from its model-free nature. The method works well for the parts of a potential covered by abundant experimental data (that is energies of rovibrational levels). However, when the experimentally determined energy levels are scarce, the inversion problem becomes ill-conditioned and its solution may become unstable, producing irregularities in a form of unphysical wiggles on the constructed potential curve. This is often pointed as the major disadvantage of the pointwise representation, compared to the analytic ones [7, 13]. In fact the ill-conditioning of the problem does not imply that a meaningful approximate solution cannot be found, but an extra care has to be taken to obtain a physically acceptable result. The SVD method chosen by us for solving the system of linear equations (9) offers a partial remedy. Also a sensible choice of a sparse grid for the pointwise potential in the regions poorly characterized by experimental data can flatten it to some extent. Recently we have proposed a simpler and more effective procedure, based on an additional constraint which imposes desired smoothness on the constructed potential [18].

A typical way to obtain a smooth fitted function $f(R, \mathbf{a})$ (\mathbf{a} stands here for a set of fitting parameters) is to add to the merit function $\chi^2(\mathbf{a})$ a regularizing functional $H(\mathbf{a})$ responsible for the smoothness of the solution and to minimize the sum $\chi^2(\mathbf{a}) + \lambda^2 H(\mathbf{a})$, where parameter λ is used to tune the degree of regularization. Since in our version of the IPA method the fitted potential is defined as a cubic spline function connecting grid points $\{R_k, U_k\}$, we define the regularizing functional as

$$H(\mathbf{U}) = \sum_j \left[U''(R_j, \mathbf{U}) \right]^2 \quad (10)$$

where $U''(R_j, \mathbf{U})$ denotes the second derivative of the potential (defined by its grid values $\mathbf{U} = \{U_1, U_2, \dots\}$) in a grid point R_j . Minimizing $H(\mathbf{U})$ of such a form sets the second derivatives of the potential close to zero, and consequently its shape becomes close to a straight line. It can be shown [18] that U'' is a linear function of the fitting parameters U_i and the regularization condition is equivalent to supplementing the system of linear equation (9) by a set of additional M equations

$$\sum_{i=0}^M \lambda L_{ji} \left[U_i^0 + \delta U(R_i) \right] = 0, \quad j = 1, 2, \dots, M \quad (11)$$

Here L_{ji} are the known numerical coefficients [18] and U_i^0 denotes the initial value of the i -th fitting parameter. When $\lambda = 0$, the system of Eq. (9) remains unchanged, that is no regularization is imposed. Increasing λ results in flattening of the potential by competition of conditions defined by (11) and (9). In general, the value of λ can be different at different grid points (*i.e.*, can depend on j), varying from zero for parts of the potential with abundant experimental data to a large value for regions poorly characterized by the experiment. It must be noted that close to the potential minimum the expression for $H(\mathbf{U})$ cannot be represented by (10) because the potential is essentially non-linear in this range. Instead $H(\mathbf{U})$ may be taken in the form

$$H(\mathbf{U}) = \sum_j \left[U''(R_j, \mathbf{U}) - U''(R_{j+1}, \mathbf{U}) \right]^2 \quad (12)$$

In this case by minimizing $H(\mathbf{U})$ one sets the third derivative of the potential close to zero, and consequently the potential close to a parabola.

The method described above has been used for construction of the potential of the double minimum $4^1\Sigma_u^+$ state in Na_2 molecule [18]. Our experimental data consisted of 277 energies of levels located in the inner well, allowing us to find the detailed shape of this well, and only 55 levels observed in the region above the potential barrier, additionally all of them corresponding to a narrow range of rotational quantum

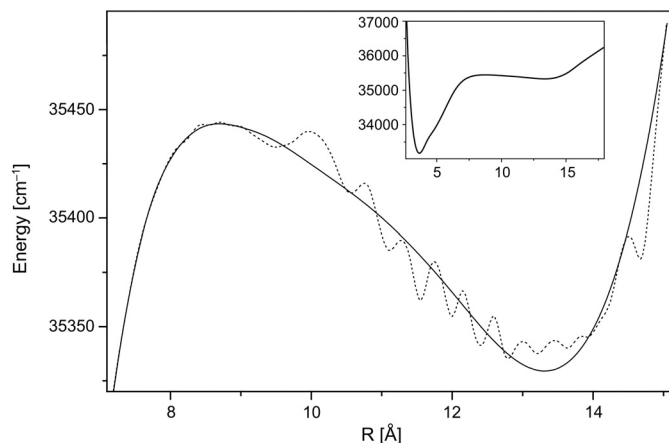


Fig. 3. The shape of the outer well of the Na_2 $4^1\Sigma_u^+$ state potential constructed with the pointwise IPA method without regularization (dashed line) and with regularization ($\lambda = 0.015$ for $R > 8.5\text{\AA}$; solid line). The whole potential curve is shown in the inset.

numbers. As the outer potential well was accessible in our experiment only through them, determination of its shape presented a particularly ill-posed problem. In general, fits without regularization led in this case to unphysical oscillations in the outer potential well, *i.e.*, in the region poorly characterized by the experimental data (Fig. 3), providing dimensionless standard error of the fit $\sigma = 0.76$. The same figure shows the result of a fit based on the same data field but including regularization of the potential curve. The parameter λ was taken as 0.015 for $R > 8.5\text{\AA}$ and fixed to zero for lower internuclear distances, in order to switch regularization only in the region related to scarce experimental data. It can be seen that the potential becomes smooth and of physically reasonable shape with only a negligible decrease of the quality of the fit ($\sigma = 0.82$).

3. Concluding remarks

In conclusion, the pointwise IPA method has proved to be a powerful tool for determination of accurate potential energy curves for electronic states of diatomic molecules, including potentials with exotic shapes where the traditional methods are not applicable. It is possible to extend the pointwise potential to the region of large internuclear distances, as discussed in [29, 30], thus enhancing capabilities of the method in determination of dissociation energies and dispersion coefficients, as well as in modelling of properties related to collisions of cold atoms and formation of cold molecules (scattering lengths, Feshbach resonances, *etc.*). The method allows to generate potentials even for coupled electronic states. In this case the respective eigenvalues can be treated as zeroth approximation energy levels and the corresponding wave functions are used to evaluate the matrix elements of the coupling

operators. Alternatively, nonadiabatic effects caused by sufficiently weak interactions between molecular states can be “absorbed” by the constructed effective potential curves. It is worth noting that our version of the IPA method is now in use by several research groups [23, 29, 31–34] and becomes gradually a standard tool in spectroscopic investigations.

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