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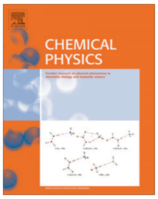

Analytical continuation in coupling constant method; application to the calculation of resonance energies and widths for organic molecules: Glycine, alanine and valine and dimer of formic acid

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ABSTRACT

The method of analytic continuation in the coupling constant (ACCC) in combination with use of the statistical Padé approximation is applied to the determination of resonance energy and width of some amino acids and formic acid dimer. Standard quantum chemistry codes provide accurate data which can be used for analytic continuation in the coupling constant to obtain the resonance energy and width of organic molecules with a good accuracy. The obtained results are compared with the existing experimental ones.

1. Introduction

The description of the resonant electron capture by molecules connected with the formation of negative ions represents still the challenge for the theory [1]. The reason is that the metastable resonance state is embedded in the continuum of scattering states, plain application of bound state techniques will inevitably lead to a neutral molecule plus a free electron. This is the reason why many theoretical papers based on standard methods failed in the calculation of vertical electron affinities of halogenated molecules. This problem has been clearly formulated by Simons and Jordan [2], stating "Because temporary anion states lie in the continuum of the neutral species plus free electron, they cannot be treated in general by means of a straightforward variational calculation". Hence there were developed different theoretical methods dealing with the temporary negative ions. A rigorous treatment of anion resonances needs, of course, quantum mechanical scattering methods such as R-matrix theory or the Kohn variation technique. Because of complicated calculations in these approaches there are applied stabilization methods to describe the negative ions. There are many variants of them; the product of all these approaches is the determination of a series of eigenvalues of the molecular Hamiltonian as a function of some scaling parameter. The drawback of these methods consists in the determination of the important physical quantity, resonance width, which is in many cases not possible to obtain. One can conclude that the calculation of resonance energies as well as resonance widths is not a routine matter; each new methodological contribution is very valuable.

To describe inelastic resonance electron-molecule processes, the knowledge of resonance energies and widths of molecular anions is required. The calculation of the parameters is not a simple task because of the nature of the resonance wave function. Several methods have been developed in the last four decades to calculate resonance energies. Let us mention just a few of them: stabilization methods [3–5], complex rotation [6] and complex absorbing potential [7,8]. In 1985, Nestmann and Peyerimhoff (NP) proposed a method [9,10] which has found widespread utilization (see, for example, Refs. [11–14]) because of its easy application and close connection to standard quantum chemistry codes. The idea is to use standard quantum chemistry codes designed to calculate bound states with variable nuclear charges. If the nuclear charges are increased by a factor λ the electron-molecule interactions become more attractive and at increasing λ over a certain limit the resonance state converts into a bound state. The calculation is repeated for several values of λ in the region where the electron is bound and a polynomial approximation is formed for the dependence of the bound-state energy $E(\lambda)$ on λ. This expression is eventually used to extrapolate to $\lambda = 0$, and this way the resonance

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energy is obtained. This approach possesses one important advantage: any quantum chemistry code can be easily modified to change the nuclear charges, and it is easy to repeat the calculation for a series of charges. This feature makes this approach very appealing but the calculation of the resonance width remains ambiguous. The ACCC method [15,16] is able to yield not only the resonance energy but also the resonance width with a very good accuracy. The method has been successfully applied to the calculation of the resonant energy and width for the molecular nitrogen negative ion [17] where also the basic ideas of the method have been introduced. In this paper we show that the application of the method to larger molecules can also provide accurate values of the resonance energies and the resonance widths. The molecules of our interest were negative ions of the simplest aliphatic amino acids (glycine, alanine and valine) and the monomer and the dimer of formic acid. In case of amino acids there are studies combining experiment and theory of the fragmentation reactions of collision products of these molecules with electron [18–20]. The center of the interest of these contributions lies in the description of the fragmentation reactions following the anion decay but the detailed characterization of ions is missing. Formic acid molecules are also interesting from the point of view of the results for vertical attachment energies with the data assigned to the monomers or dimers. There is a spectrum of the vertical attachment energy (VAE) values obtained experimentally or on the theoretical level [21–24]. It gives the reason for us to apply the method for larger molecules to find the differences between two structures and to assign the value of the vertical attachment energy to the true structure.

2. Computational details and data production

The evaluation of the energies of the smallest aliphatic amino acids anions for glycine, alanine and valine as well as the treatment of monomer and dimer anions of the formic acid have been performed using of Gaussian 03 program package [25]. Geometries of the molecules were optimized with MP2/6-311+G(2d,2p) [26–30]. The optimized geometries were then used for single point calculations at the MP2, spin-component scaled MP2 (SCS-MP2) [31], MP4 [32], QCISD(T,E4T) [33–35] and OVGF (Outer Valence Green Function) [36–43] levels of the theory for the formic acid monomer and dimer as well as at the MP2 and OVGF levels of the theory for the three studied amino acids. These methods were combined with 6-311+G(2d,2p) and 6-311++G(2df,2pd) basis sets [44–47]. For the monomer structure of the formic acid the OVGF method with full 6-311+G(2d,2p) basis set, frozen core aug-cc-pVTZ and again full aug-cc-pVQZ basis sets [48–53] has been used to determine the energy of the resonant orbital. Moreover more accurate ab initio methods MP4 and QCISD(T,E4T) has been used with aug-cc-pVTZ basis set also. For the last two methods as well as for the MP2 method the set of calculations has to be doubled for the neutral and anionic states from which the resonant energy was evaluated as the difference of the total energies of these two states. For the dimer structure we have performed calculations with the previous methods and basis sets as for the monomer except the MP4 with aug-cc-pVTZ calculations and OVGF with full aug-cc-pVQZ calculations. Amino acids of glycine, alanine and valine have been treated with MP2 and OVGF methods together with the 6-311++G(2df,2pd) basis set. To describe the anions we stabilized with the modified nuclear charges the resonant orbital where the extra electron is attached. We performed a modification of all nuclear charges of the molecules. To decrease the computational costs we have divided the computational procedure into two parts. With a defined step 0.001 the λ parameter was varied from 0.006 up to 0.05. In the second part we increased the step to 0.002 and varied the λ parameter from 0.05 up to 0.1. This approach resulted in 70 values for λ parameter where for each λ the total energies of neutral and anionic state have been calculated.

2.1. ACCC method

The method of the analytical continuation in the coupling constant (ACCC) as applied to molecular resonances has been described in detail in Ref. [17]. For its original version we refer the readers to Ref. [15]. The essence of the method is to transform the problem of resonance calculation to much easier problem of bound state energy calculation by introducing a perturbation. The perturbation is eventually eliminated and the resonance energy and width obtained by means of the analytical continuation in the parameter describing the strengths of the perturbation. This is done by means of Padé approximation. In this work we will follow the work of Nestmann and Peyerimhoff [9,10] and use the Coulomb potential for the analytical continuation. This is not the best choice from the point of the scattering theory but it is very convenient for the use of commercial quantum chemistry codes.

The ACCC method is based on the following observation [16,15,54]: It is well known that if we make the Hamiltonian H describing our system more attractive by adding an attractive perturbation λV,

$$H \rightarrow H + \lambda V, \qquad (1)$$

the bound states get more bound and resonances move closer to the origin. At some value of λ=λ_0 both resonance poles merge and transform into a pair of bound and virtual states. If we calculate bound state energy $E(\lambda)$ for several values of λ we can construct a frequently used polynomial approximation to $E(\lambda)$, e.g.,

$$E(\lambda) = E_0 + E_1\lambda + E_2\lambda^2 + \cdots \qquad (2)$$

and extrapolate this function to $\lambda \rightarrow 0$. But since $E(\lambda)$ attains only real values – the bound state energies are of course real – the result of the extrapolation is a real quantity which in some sense represents the resonance energy but gives no information on the imaginary part of the resonance energy. As shown in Ref. [54] and references therein the function $k(\lambda),\ E(\lambda) = k^2(\lambda)$, has for nonzero angular momentum l a singularity at a point λ_0 where $k(\lambda_0) = 0$. The singularity is of the square root type

$$k(\lambda) \approx \sqrt{\lambda - \lambda_0} \quad \text{at} \quad \lambda \approx \lambda_0. \qquad (3)$$

This indicates that the expansion Eq. (2) cannot represent the resonance energy for λ below λ_0. In accordance with [54] we represent $k(\lambda_0)$ in the form of Padé approximation in a new variable y

$$k(y) \approx k^{[N/M]}(y) = \frac{P_N(y)}{Q_M(y)}, \quad y = \sqrt{\lambda - \lambda_0}, \qquad (4)$$

where $P_N(y)$ and $Q_M(y)$ are polynomials

$$P_N(y) = \sum_{i=0}^{N} p_i y^i, \quad Q_M(y) = 1 + \sum_{i=0}^{M} q_i y^i. \qquad (5)$$

This representation takes into account the singularity at $\lambda = \lambda_0$ exactly and the Padé approximation carries out the analytical continuation [54]. At values $\lambda < \lambda_0,\ k(\lambda)$ gets complex and the resonance energy acquires its complex part. To calculate the bound state energies and their square integrable wave functions is now a routine task and many commercial programs are available. This makes this method very attractive.

The coefficients of the polynomials in Eq. (5) are determined as the least square approximation to the data obtained by minimizing the χ^2 functional

$$\chi^2 = \sum_{l=1}^{L} \frac{1}{\epsilon_l^2} \left| \frac{P_N(x_l)}{Q_M(x_l)} - f_l \right|^2. \qquad (6)$$