On the calculation of resonances by means of analytic continuation in coupling constant

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Abstract. The method of analytic continuation in the coupling constant in combination with the use of statistical Padé approximation designed to determine resonance parameters is introduced. It is shown that standard quantum chemistry codes provide accurate data which can be used for the process of analytic continuation in coupling constant. Resonance parameters, both the energy and the width, can be inferred for real molecules with accuracy comparable to other more elaborated methods.

1. Introduction

In plasma physics many scattering processes are responsible for the determination of the state of the plasma. In addition to elastic scattering the processes of dissociative electron attachment (DA)

\[ e + H_2(v_i, J_i) \rightarrow H + H^- , \]  

(1)

associative detachment (AD)

\[ H + H^- \rightarrow e + H_2(v_f, J_f) , \]  

(2)

vibrational excitation (VE)

\[ e + H_2(v_i, J_i) \rightarrow e + H_2(v_f, J_i) \]  

(3)

and dissociative recombination (DR)

\[ e + H_2^+ \rightarrow H + H \]  

(4)

are important. These processes play a decisive role in many other fields. In astrophysics, for example, it is assumed [1] that the process of AD is responsible for the creation of the hydrogen molecule at early stages of the development of the Universe. The existence of the H₂ molecule represents a very efficient cooling mechanism of the hot materials which eventually leads to the creation of stars, galaxies, etc. It was suggested [2, 3] that DA to vibrationally excited molecular hydrogen plays an important role in molecular activated recombination in fusion divertor plasmas. This process is also believed to be the primary source of negative-ion production in low-density hydrogen plasmas, see e.g. [4, 5, 6]. All the processes mentioned above are of resonance nature: they are efficient in a restricted range of energy. This is demonstrated...
Figure 1. \( \text{H}_2 \) dissociative electron attachment cross section. Feature A: \( ^2\Sigma_u^+ \) shape resonance, feature B: \( ^2\Sigma_g^+ \) shape resonance, feature C: formation of excited atomic state \( e + \text{H}_2 \rightarrow \text{H}^- + \text{H}(2s) \).

In Figure 1 where the dissociative attachment cross section is shown for the \( e - \text{H}_2 \) system. Each peak in the figure corresponds to a different resonance. For determination of the cross sections it is important to know the resonance energy and its width. It is the purpose of this note to describe a simple method for determination of those parameters.

2. Determination of resonance parameters

In practical applications several more or less accurate definitions of a resonance were used. For example one can fit measured scattering cross section by the Breit-Wigner or Fano formula and derive the resonance parameters. This works well for narrow resonances with small background. Mathematically correct definition of a resonance is related to the S-matrix. Let us assume that the interaction between colliding particles is described by a potential \( U(r) \) which is negligible at large distances \( U(r) = 0, r > R \). Then the solution of the Schrödinger equation, \( \psi_l(r) \) has the asymptotic form (for zero angular momentum this expression is exact for any \( r \geq R \)).

\[
\psi_l(r) \approx N (e^{-ikr} + S_l(k)e^{ikr}), \quad r \to \infty.
\] (5)

The function \( S_l(k) \) - the S-matrix - is known to have poles in the complex plane of \( k \) [7]. If the pole occurs on the positive imaginary axis, \( k = i\kappa, \kappa > 0 \), the wave function \( \psi_l(r) \) behaves at large distances as

\[
\psi_l(r) \approx e^{-\kappa r}
\] (6)

and describes bound states. For poles at negative imaginary axis, \( k = -i\kappa, \kappa > 0 \) we have

\[
\psi_l(r) \approx e^{\kappa r}.
\] (7)
This pole describes the so-called virtual states. Finally, poles at $k = k_1 - ik_2$, $k_1, k_2 > 0$ describe resonances which we are looking for. The resonance wave function behaves at large distances as

$$\psi_l(r) \approx e^{ik_1r} e^{ik_2r},$$

i.e., the resonance wave function oscillates and its amplitude exponentially increases at increasing $r$. This feature indicates that to calculate the resonance wave function is a difficult task whereas the calculation of bound states is easy because the wave function is so simple.

3. **Analytical continuation**

In what follows we introduce a method which for determination of resonance parameters uses only bound state energy data. The method - the so-called method of analytical continuation in coupling constant (ACCC) is based on the following observation: It is well known that if we make the potential $U(r)$ describing our system more attractive by adding a perturbation $\lambda V(r)$,

$$U(r) \rightarrow U(r) + \lambda V(r),$$

the bound states get more bound and resonances move closer to the origin. At some value of $\lambda = \lambda_0$ 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 $\lambda$ we can construct a frequently used polynomial approximation to $E(\lambda)$, e.g.,

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

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. It is a common situation in physics that some quantity which can be measured or calculated in a restricted range of some parameter is required outside this range. Let us consider for example the function $\frac{1}{1-x}$ represented as a power series

$$f(x) = \frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots.$$  (11)

Since the radius of convergence of this series is equal to 1, it can be used in practice only for $x < 1$. The radius of convergence is determined by the nearest singularity, here the simple pole at $x = 1$. There exist several methods how to use the expansion (11) even at $x > 1$. Here we mention just one of the approaches - the Padé approximation. As Padé approximation [8] we mean the representation of a function $f(x)$ in the form

$$f(x) \approx f^{[N,M]}(x) = \frac{P_N(x)}{Q_M(x)},$$

where $P_N(x)$ and $Q_M(X)$ are polynomials

$$P_N(x) = \sum_{i=0}^{N} p_i x^i, \quad Q_M(x) = 1 + \sum_{i=1}^{M} q_i x^i.$$  (13)

Three ways how to determine the coefficients of the polynomials are in common use. As suggested by Padé the function $f^{[N,M]}(x)$ can be expanded into a Taylor series and the obtained
coefficients compared with the expansion coefficients of the function \( f(x) \). If this is done say for \( N = 1, M = 1 \) we obtain

\[
f^{[1,1]}(x) = \frac{1}{1 - x},
\]

i.e. from the knowledge of several expansion coefficients we obtain the exact functional form of \( f(x) \). The obtained expression can now be used even for \( x > 1 \). This is not fortuitous, it is known that the Padé approximation carries out the analytical continuation automatically [8].

The Padé approximation discussed above, the so-called Padé I approximation, is not useful for practical application. The reason is that our data are always of limited accuracy. Instead we propose to use the so-called statistical Padé approximation, Padé III approximation, defined as follows: again

\[
f(x) \approx f^{[N,M]}(x) = \frac{P_N(x)}{Q_M(x)},
\]

but the coefficients of the polynomials are determined as the least square approximation to the data obtained by minimizing the \( \chi^2 \) functional

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

In the above equation \( \{\epsilon_l\} \) indicates the inaccuracy of the data used. The calculation of the Padé III approximation is a nonlinear problem; an efficient solution is described in [8] and [9].

As discussed in [8] the Padé approximation has two very important features (among others): 1. as already mentioned above it carries out the analytical continuation automatically; and 2. it is flexible enough to approximate functions with singularities (poles and cuts).

### 3.1. Analytic continuation in the coupling constant

As shown in [8] and references therein the function \( k(\lambda), E(\lambda) = k^2(\lambda), \) has for nonzero angular momentum \( l \) a singularity at a point \( \lambda_0 \) where \( k(\lambda_0) = 0 \). The singularity is of the square root type

\[
k(\lambda) \approx a\sqrt{\lambda - \lambda_0} + ....,
\]

This indicates that the expansion (10) cannot represent the resonance energy for \( \lambda \) below \( \lambda_0 \). In accordance with (17) we represent \( k(\lambda) \) in the form of Padé approximation in a new variable \( y \)

\[
k(y) \approx \frac{P_N(y)}{Q_M(y)}, \quad y = \sqrt{\lambda - \lambda_0}.
\]

This representation takes into account the singularity at \( \lambda = \lambda_0 \) exactly and the Padé approximation carries out the analytical continuation. 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. This ACCC method was proposed in the field of nuclear physics by Krasnopolsky and Kukulin [10] and [11] in seventieths and is in detail described in the book [8]. This approach has found applications mostly in nuclear physics, see e.g. [12], [13], [14]. In those applications the so called Padé II approximation was used which is based on interpolation of the data. Because interpolation is sensitive to small changes in the data a high accuracy of the input data is required [15]. This limits the use of ACCC mostly to model analytic problems.

In this work we will follow the work of Nestmann and Peyerimhoff [16] 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.
3.2. Determination of the parameter $\lambda_0$.
Correct determination of the branch point $\lambda_0$ is of decisive importance for the accuracy of the ACCC approach. A possible way how to find it is proposed in [8]. For nonzero values of the angular momentum (and this is the most important case) the bifurcation point $\lambda_c$ coincides with $\lambda_0$, $\lambda_c = \lambda_0$. Since molecular s-wave resonances are very rare we restrict here to the case of nonzero angular momentum. A rough approximation of $\lambda_0$ can be obtained by simple extrapolation of $\lambda(E)$ to zero, $E \rightarrow 0$. Here, however, when using the statistical Padé approximation, we have a new tool at hand: provided the data are accurate enough the function $\chi^2$ as a function of the parameter $\lambda_0$ possesses a sharp minimum at the true value of $\lambda_0$, see [17]. In addition the knowledge of $\chi^2(\lambda_0)$ can serve as a tool to select an optimal value of the order $N/M$ of the Padé approximation. If $N$ and $M$ are too high the function $\chi^2(\lambda_0)$ becomes erratic because the approximation reproduces the noise.

4. Application
The ACCC approach was recently successfully applied to the treatment of $^2\Pi_g$ state of $N_2^-$ [18]. It was shown there that the resonance width was determined with a very high accuracy $\approx 50$ meV and the resonance energy $\approx 100$ meV. Preliminary results were also obtained for CO$^-$ and H$_2^-$ resonance states. The $^2\Sigma_u$ of H$_2^-$ resonance is an example of a very broad resonance which is hardly to be discerned in scattering calculation [19]. The bound state data available for this state did not allow us to use higher order Padé approximation; only the lowest [1/1] approximation provided stable results. For more accurate determination of the resonance parameters of this state more extensive data are needed. In Figure 2 we plot the results of the analytical continuation by means of Padé 1/1 for this state. The bound state energy is positive in this Figure, the calculated resonance energy negative. In Figure 3 we compare the present results with other calculations, [20] and [21].

Figure 2. Analytic continuation (Padé 1/1) for the $^2\Sigma_u^+$ state of H$_2^-$: Solid line - the resonance energy, the dashed line - the resonance width, crosses - the calculated bound state energies.
5. Conclusions

We conclude that the ACCC method can be applied to the calculation of low-energy electron-molecule resonances even while using the long-range Coulomb potential for the transformation of resonances into bound states. The obtained data agree well with the results of other, often much more elaborate, methods [18]. The great advantage of the present method is that, without changes, it could be used also to polyatomic molecules relevant to plasma physics. This will be discussed in our future publications. It is however necessary to say that the method has its limitations. The most important limitation is that in the present form it is applicable to low-energy isolated shape resonances only. If the resonance is located very far from the origin (e.g. very broad resonance) the method loses its accuracy because the continuation must be done to very large distances.

Acknowledgments

This work was supported by Zámr MSM0021620860, by the Center of Theoretical Astrophysics LC06014 of the Ministry of Education, Youth and Sports of the Czech republic and the COST Action CM0601 ECCL Electron Controlled Chemical Lithography No. OC09079.

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