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Shape resonances of Be$^-$ and Mg$^-$ investigated with the method of analytic continuation

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The regularized method of analytic continuation is used to study the low-energy negative-ion states of beryllium (configuration $2s^2\varepsilon p\,^2P$) and magnesium (configuration $3s^2\varepsilon p\,^2P$) atoms. The method applies an additional perturbation potential and requires only routine bound-state multi-electron quantum calculations. Such computations are accessible by most of the free or commercial quantum chemistry software available for atoms and molecules. The perturbation potential is implemented as a spherical Gaussian function with a fixed width. Stability of the analytic continuation technique with respect to the width and with respect to the input range of electron affinities is studied in detail. The computed resonance parameters $E_r = 0.282$ eV, $\Gamma = 0.316$ eV for the $2p$ state of Be$^-$ and $E_r = 0.188$ eV, $\Gamma = 0.167$ for the $3p$ state of Mg$^-$ agree well with the best results obtained by much more elaborate and computationally demanding present-day methods.

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I. INTRODUCTION

Resonances in electron-atom or electron-molecule scattering, also addressed as transient negative ions, have attracted attention over the last decades. It is because these temporary states provide a pathway for electron-driven chemistry via dissociative electron attachment (DEA) and therefore, applications can be found in chemistry of the planetary atmospheres [1], nanolithography in microelectronic device fabrication [2,3], and in cancer research where these states provide a mechanism for DNA damage by low-energy electrons [4,5].

Accurate calculation of energies and lifetimes of the resonances represents a challenging task that is more complicated than the determination of energies of the bound atomic or molecular states. Temporary negative ions differ from the bound states in two important respects: (i) they are not stable and decay into various continua, (ii) corresponding poles of the S matrix are complex and they are expressed by $E = E_r - i\Gamma/2$. Numerous studies have been published that discuss several methods for determination of the resonance energies and widths. In scattering calculations, the presence of the resonances leads to enhanced cross sections and sharp changes in phases of the continuum wave functions. Resonance positions and widths are then determined by Breit–Wigner fits of the eigenphase sums or their energy derivatives (time-delay method) [6,7]. Stabilization methods [8–11] search for a region of stability of the energies with respect to different confining parameters. The Stieltjes imaging technique [10] allows us to represent the resonant state by a square-integrable basis and the width is defined by the resonance-continuum coupling. Complex rotation methods [12–14] and the methods employing complex absorbing potential [15,16] compute complex resonant energy as an eigenvalue of a complex, non-Hermitian Hamiltonian.

Recently, the method of analytic continuation in coupling constant (ACCC) [17–19] has been applied to several molecular targets, such as N$_2$ [20,21], ethylene [22,23], and amino acids [24]. Furthermore, the known low-energy analytic structure of the resonance was incorporated into the inverse ACCC (IACCC) method providing so-called regularized analytic continuation (RAC) method. The RAC method was successfully employed for determination of π^* resonances of acetylene [25] and diacetylene [26] anions, proving that the ACCC method can yield accurate resonance energies and widths for various molecular systems using data obtained with standard quantum chemistry codes.

Common features of all methods of analytic continuation is an application of the perturbation potential λV to the multi-electron Hamiltonian H, i.e., $H \to H + \lambda V$. The role of this attractive perturbation is to transform the resonant state into a bound state. Although the RAC method was developed for strictly short-range perturbations V, authors were able to successfully use the Coulomb potential in its stead [25,26]. This obvious inconsistency can yield reasonable results, because in practical applications the perturbation potential is often projected onto a finite set of short-range basis functions, e.g., Gaussian functions used by the quantum chemistry software. However, weakly bound states thus obtained need to be examined carefully because they may, in fact, be Rydberg states supported by the basis and the long-range tail of the Coulomb perturbation V [26]. Such states need to be excluded from the continuation procedure because they do not represent a resonance transferred to a bound state. To avoid such complications, in the present study we adopt a short-range

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perturbation potential in the form of a Gaussian function,

$$V(r) = -e^{-\gamma r^2}. \tag{1}$$

This choice of the perturbation was recently evaluated by White *et al.* [21] and applied to the well-known $^2\Pi_g$ resonance of N_2^-. Furthermore, Sommerfeld and Ehara [27] introduced another short-range potential, termed the "Voronoi soft-core potential," which they successfully used to analyze the $^2\Pi_u$ resonance of CO_2^-.

The present analysis of the Gaussian perturbation potential (1) will be carried out for expectedly simpler problems—atomic shape resonances of beryllium and magnesium. Both atoms are known to possess a p-wave shape resonance very close to the elastic threshold. While in the case of the Mg^- the agreement between the available computed resonance parameters [28–30] and the experimental data [31,32] is quite good, the situation is very different for the beryllium atom. There has been a great number of theoretical studies [33–45] aiming to numerically characterize the Be^- $2s^2\varepsilon p\,^2P$ resonance, with various levels of success. Table III in Ref. [43] clearly summarizes that the theory of the last four decades predicts the resonance position between 0.1 and 1.2 eV and the resonance width between 0.1 and 1.7 eV. Even the most recent calculations differ by a factor of about three for the two resonant parameters. Moreover, no experimental data are available for the Be^- resonance that could narrow the spread of all the available theoretical predictions.

Convergence patterns shown in Refs. [43,44] demonstrate that the Be^- resonance may be very sensitive to an accurate description of the electronic correlation energy. Therefore, in the present study we employ coupled-clusters (CCSD-T) and full configuration-interaction (FCI) methods for the perturbed Be^- electron affinities that will then be continued in the complex plane by the RAC method. The basic ideas of the RAC method are given in the Sec. II. A quick summary of the quantum chemistry details is presented in Sec. III. In Sec. IV we analyze the stability and accuracy of the RAC method with the Gaussian perturbation potential (1). The conclusions then follow.

II. METHOD OF REGULARIZED ANALYTIC CONTINUATION

The RAC method represents a very simple method for calculating the resonance energies and widths and which embraces all known analytical features of the coupling constant λ near the zero energy [26]. The method works as follows:

(1) The atom or molecule is perturbed by an attractive interaction V multiplied by a real parameter λ

$$H_{\text{neutral}} \to H_{\text{neutral}} + \lambda V, \tag{2}$$

and bound-state energies E_i^N of the neutral state are calculated for a set of values λ_i.

(2) The same procedure is carried out for the corresponding negative ion:

$$H_{\text{ion}} \to H_{\text{ion}} + \lambda V, \tag{3}$$

where the bound-state energies E_i^I are calculated for the same values of λ_i. In the present study the two energies E_i^I and E_i^N are the ground-state energies for the respective cases.

(3) Both energies are subtracted, forming the electron affinity in the presence of the perturbation potential V:

$$E_i^N - E_i^I = E_i = \kappa_i^2. \tag{4}$$

The new set of data points $\{\kappa_i,\lambda_i\}$ is then used to fit the function

$$\lambda(\kappa) = \lambda_0 \frac{(\kappa^2 + 2\alpha^2\kappa + \alpha^4 + \beta^2)(1 + \delta^2\kappa)}{\alpha^4 + \beta^2 + \kappa[2\alpha^2 + \delta^2(\alpha^4 + \beta^2)]}. \tag{5}$$

It is represented as a Padé 3/1 function and it defines the level of complexity of the pole behavior at the low bound or continuum energies. We call it the RAC [3/1] method. The origin of its form and the fitting formulas for the [2/1], [3/2], and [4/2] methods can be found in Ref. [25]. The parameters of the [3/1] fit; namely, α, β, δ, and λ_0 are found by minimizing the χ^2 functional,

$$\chi^2 = \frac{1}{N}\sum_{i=1}^{N} \frac{1}{\varepsilon_i^2} |\lambda(\kappa_i) - \lambda_i|^2, \tag{6}$$

where N denotes the number of the points used, while κ_i and λ_i are the input data. Once an accurate fit is found, only the parameters α and β determine the resonance energy

$$E_r = \beta^2 - \alpha^4 \tag{7}$$

and the resonance width

$$\Gamma = 4\beta\alpha^2. \tag{8}$$

The role of the parameter δ is to describe a virtual state with $E_v = -1/\delta^4$. Even in the case in which the studied system does not possess a virtual state, this parameter represents a cumulative effect of the other resonances and other poles not explicitly included in the model. The weights ε_i (accuracy of the data) in Eq. (6) are generally unknown. The calculation can be routinely performed with constant $\varepsilon_i = 1$ or, if the importance of the data points closest to the origin needs to be stressed, an increasing-weight sequence (e.g., $\varepsilon_i = i$) can be used.

Our experience shows that, for realistic (not model) data obtained by standard quantum chemistry approaches (CCSD-T or MRCI), the higher RAC approximations ([3/2] and [4/2]) do not provide an essential improvement in the quality of the fit represented by χ^2. In addition, the higher RAC orders are more influenced by the noise of the data than the lower approximations and, when the number of fitting parameters gets large, the optimization often ends in a local minimum. For these reasons the RAC [3/1] approximation is used in the present analysis because it constitutes the best compromise between the accuracy and the stability of the calculation.

The RAC method has been recently critically evaluated by White *et al.* [21]. The authors tested three types of perturbation potential:

$$V(r) = -\frac{1}{r}, \tag{9}$$

$$V(r) = -\frac{e^{-\gamma r^2}}{r}, \tag{10}$$

$$V(r) = -e^{-\gamma r^2}, \tag{11}$$

and they suggested that the attenuated Coulomb potential (10) is the best choice of the three options. They also concluded that the Gaussian potential (11) does not represent a good choice for the RAC method. All these potentials are easily implemented into the standard quantum chemistry codes. The aim of the present contribution is twofold:

(1) to explore application of the Gaussian-type perturbation and to find the parameters that allow accurate extraction of the resonance data with the RAC method;

(2) to demonstrate that the RAC method can be applied with success to low-lying atomic shape resonances.

Before applying the RAC method one must consider two important issues:

(1) The first issue is the choice of the perturbation potential, i.e., in the present context the choice of the exponent γ in Eq. (11). Presently, there exist no general rule, no guide that helps us to choose the perturbation potential. Therefore, it is necessary to perform calculations for a set of values of the parameter γ to find an optimal choice. If the optimal range of values is found, it is reasonable to expect that the obtained resonance data should stabilize in such a range, because the exact function $\lambda(\kappa)$ gives the same resonance data for every choice of the perturbation potential. Since the present [3/1] RAC function is only approximative, one can only expect an existence of a plateau that gives approximative values of the resonance parameters.

(2) The RAC method represents essentially a low-energy approximation to the exact function $\lambda(\kappa)$. It is therefore obvious that the method should be used in a range of energies (or momenta) limited by some maximal energy E_M. Our empirical experience shows that $E_M \sim 8E_r$ (E_r is the sought resonance energy) gives a reasonable estimate for the range of energies.

III. ELECTRON AFFINITIES

Ab initio calculations for the electron affinities $E_i(\lambda_i)$ in presence of the external Gaussian field (11) were carried out by using the CCSD-T [46,47] and FCI methods as implemented in the MOLPRO 10 package of quantum-chemistry programs [48]. The core of the basis set employs Dunning's augmented correlation-consistent basis of quadruple-zeta quality aug-cc-pVQZ [49] for both atoms, Be and Mg. This basis set was additionally extended in an even-tempered fashion by $2s$-, $2d$-, $2f$-,and $2g$-type functions and $6p$-type functions.

Calculations for the neutral atoms and corresponding negative ions used the same basis sets and the same correlation methods (CCSD-T or FCI). Typical dependence of the electron affinities on the external field (11) is shown in Fig. 1 for both negative ions, Be$^-$, and Mg$^-$, and in the range of energies used for the present analytic continuation. Figure 1 yields the following observations:

(1) As expected, the weaker perturbation potential with $\gamma = 0.035$ requires a stronger scaling parameter λ to achieve the same binding negative-ion energies as the perturbation with $\gamma = 0.025$.

(2) Surprisingly, a larger scaling parameter (stronger perturbation) is necessary to bind the Mg$^-$ resonance that lies closer to the zero when compared with the Be$^-$ resonance (as will be seen below). Such behavior may be caused by the spatial extent of the Mg^-3p resonant wave function when compared with the reach of the $2p$ wave function of the Be$^-$ ion.

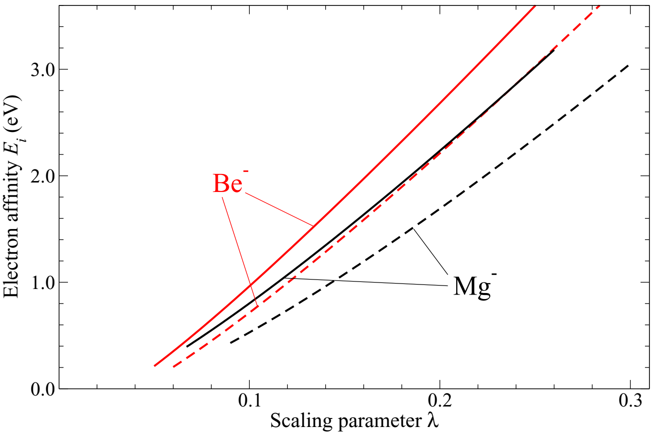

FIG. 1. Electron affinities of Be$^-$ and Mg$^-$ ions under the influence of the perturbation potential (11). Full lines are shown for the exponent $\gamma = 0.025$, while the broken lines are for $\gamma = 0.035$. Red color (light gray) describes the Be$^-$ ion and the black color is for the Mg$^-$.

(3) The lowest binding energies are not included in the continuation input data because of the difficulties we encountered while using the quantum chemistry software. The Hartree–Fock method is known to destabilize in very diffused basis sets; however, low binding energies are inaccurate if a more compact basis is used.

Most of the present results were obtained with the CCSD-T method. However, once the the optimal exponent γ (see Sec. IV) was found for the beryllium atom, the affinity curve shown in Fig. 1 was also recomputed with the expensive FCI method and the basis as described above.

IV. RESULTS

As discussed in Sec. II, our goal is to search for regions of stable results with respect to the two optimization parameters.

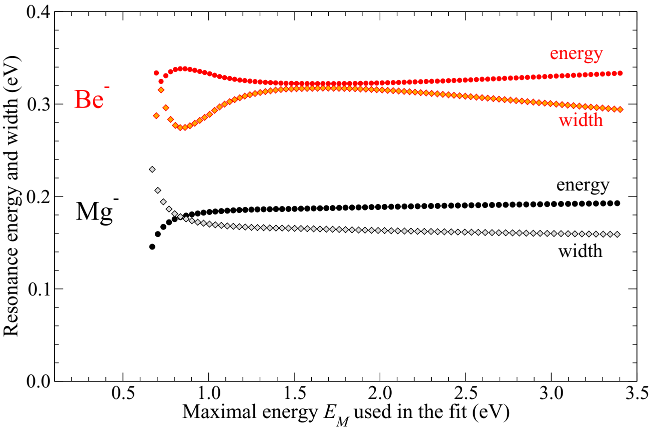

FIG. 2. Resonance energy (shown as circles) and width (displayed as diamonds) calculated for Be$^-$ and Mg$^-$ as functions of the energy extent defined by the maximal energy E_M. The exponents γ are fixed at $\gamma = 0.035$ for Be$^-$ and $\gamma = 0.025$ for Mg$^-$.

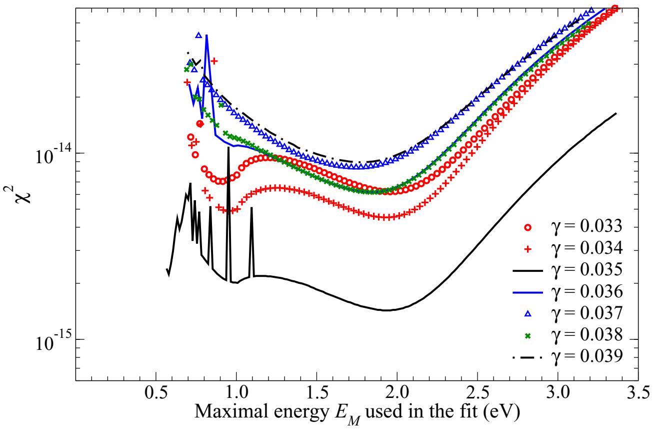

FIG. 3. Quality of the RAC fit for the resonance of Be$^-$ as a function of the maximal energy. Exponents γ range from 0.033 to 0.039 bohr^{-2} and the increasing-weight set $\varepsilon = i$ is used.

First is the range of the input electron affinities defined by maximal affinity E_M. The second parameter, the exponent γ in Eq. (11), defines the shape of the perturbation potential. Typical dependence of the resonance parameters on the maximal energy is shown in Fig. 2 for the fixed γ parameters. It is clear that the stability is little worse for the Be$^-$ ion when compared with the Mg$^-$ ion. However, it is possible to narrow the spread of the obtained resonance data by considering the value of χ^2 defined by Eq. (6). Figure 3 shows the dependence of the χ^2 quantity on the maximal energy E_M for several exponents γ. Each of the data sets exhibits a pronounced minimum just under 2 eV. This minimum allows the application of the condition of the best fit. Such a restriction leads to a well-defined E_M for each choice of the perturbation parameter γ producing the data sets shown in Fig. 4. For beryllium the resonance position and width stabilize for $\gamma > 0.02$. Moreover, Fig. 3 suggests that the best fit is obtained for $\gamma = 0.035$, resulting in $E_r = 0.323$ eV and $\Gamma = 0.317$ eV. To estimate the accuracy of the correlation energy provided by the CCSD-T method we also recomputed this final result with the FCI method. The FCI affinities yield $E_r = 0.282$ eV and $\Gamma = 0.316$ eV. A detailed summary of the available theoretical results for the Be$^-$ resonance was presented in Table III of Ref. [43]. A comparison with the most recent computations will be given in Sec. V.

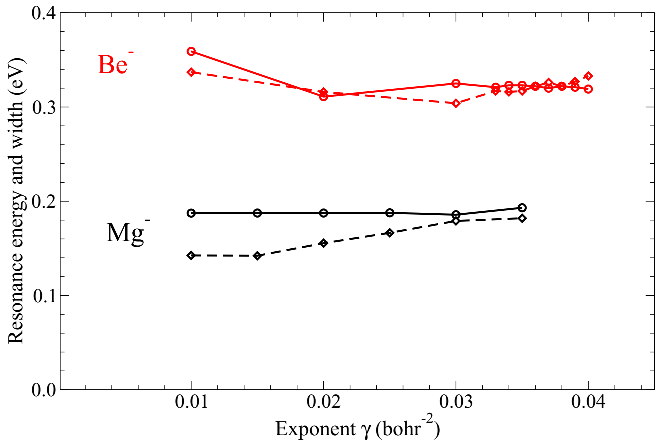

FIG. 4. Resonance energy E_r (circles connected by full lines) and the resonance width Γ (diamonds connected by dashed lines) as functions of γ parameter of the perturbation potential.

TABLE I. Comparison of available data for the resonance energy E_r and the resonance width Γ for the $3s^2\varepsilon p\,^2P$ state of atomic magnesium.

Method	Resonance energy E_r (eV)	Resonance width Γ (eV)
Model potential [28]	0.37	0.10
Model potential [30]	0.161	0.160
Complex rotation [29]	0.08	0.17
Stabilization [50]	0.14	0.08
Stabilization [45]	0.22	0.24
Complex SCF [51]	0.50	0.54
Finite elements [52]	0.159	0.12
Experiment [31]	0.15 ± 0.03	∼0.14
Recommended value [32]	0.15	0.16
Present RAC	0.19	0.16

In the case of the magnesium ion, the resonance energy is very stable over the whole range of examined perturbation parameters γ. However, the width exhibits a weak dependence on the exponent γ. This feature may indicate that the low-order RAC method is inadequate for the Mg$^-$ resonance. Nonetheless, after applying similar procedure as in the case of beryllium, we found that the best fit is obtained for $\gamma = 0.025$, giving $E_r = 0.188$ eV and $\Gamma = 0.167$ eV. The available data for the Mg$^-$ resonance are summarized in Table I. The presently computed resonance energy is about 40 meV higher that the experimental value of Burrow *et al.* [31,53]. Such a discrepancy may have several possible reasons:

(1) The experimental resolution is about 30–40 meV [31].

(2) The discrepancy between the correlation energies of the CCSD-T and FCI methods and the present basis set is about 41 meV for the electron affinity of the beryllium atom. Similar difference can also be expected for the magnesium. Moreover, weaker stability of Γ with respect to the perturbation potential (shown in Fig. 4) indicates that higher-order continuation may be necessary.

(3) The experimental resonance energy [31] was determined from the minimum of the transmitted current, whereas present method defines the resonance energy from a pole of the S matrix. The two definitions give similar results for a narrow resonance ($\Gamma < E_r$), but for for a broader resonance ($\Gamma \geqslant E_r$), as in the present case, the results may differ. For example, the minimum of the transmitted current on the rising background [31] is shifted to lower energies. On the other hand, in the case of the Be$^-$ resonance, the maxima of the computed cross sections are slightly shifted to the higher energies because of the rising background contributions [44].

V. CONCLUSIONS

The method of regularized analytic continuation (RAC) was applied to the lowest shape resonances of beryllium and magnesium atoms. The technique is based on the analytic continuation of the electron affinities and, therefore, is capable of providing the resonance parameters for the highest correlation treatment that is computationally feasible in the bound-state calculations of the corresponding negative ions. On the other hand, the RAC method, being essentially a low-energy method, is not well suited to describe resonances for higher collision energies (above ~5 eV). However, this energy restriction should not affect current considerations because both examined resonances are very close to the elastic thresholds.

The present study confirms the observations of White *et al.* [21], in which the authors state that the Gaussian perturbation potential is more difficult to apply than potentials possessing the Coulomb singularity. It has been shown in the case of a model potential [21] that the trajectory of the resonant pole is more complicated for the Gaussian perturbation. In the present study we have shown that, in order to obtain stable results, the RAC method must be restricted to fairly low electron affinities and a careful analysis of the results with respect to the width of the perturbation potential must be carried out.

This procedure allowed us to apply the RAC method to one of the remaining enigmas among shape resonances of small atoms; the $2s^2\varepsilon p\,{}^2P$ resonance of Be$^-$. To the best of our knowledge no experimental data are available for this resonance. The important role of the correlation energy in this system creates a challenging task for the theory, albeit the fact that Be$^-$ possess only five electrons. Consequently, about two dozen theoretical predictions (found in Refs. [33–44]) do not result in any kind of a consensus. Two methods with a high level of correlation descriptions, the CCSD-T and FCI methods, were applied in the present study. While the position of the resonance shifts to the lower energies by about 41 meV for the more accurate FCI method, the resonance width was found to be insensitive to the correlation treatment. Presently calculated FCI resonant energy $E_r = 0.282$ eV and width $\Gamma = 0.316$ eV are in a good agreement with older complex CI results of McNutt and McCurdy [37] that predict $E_r = 0.323$ eV and $\Gamma = 0.296$ eV, and recent stabilization calculations of Falcetta *et al.* [45] claiming $E_r = 0.33$ eV and $\Gamma = 0.40$ eV. Moreover, the scattering calculations of Zatsarinny *et al.* [44] determined the resonance with $E_r = 0.31 \pm 0.04$ eV and $\Gamma = 0.40 \pm 0.06$ eV, again in good agreement with the present results. However, another set of recent calculations by Tsednee *et al.* [43] place the resonance at $E_r = 0.756$ eV and $\Gamma = 0.874$ eV. These calculations employ the multiconfiguration self-consistent field (MCSCF) method to describe the electronic correlation, while the resonant state is confined by the complex scaling technique.

In case of the $2s^2\varepsilon p\,{}^2P$ resonance of Mg$^-$, a comparison with experiment is available. Although the present calculations determine the resonance about 40 meV higher than the experiment [31], they still exhibit the best agreement with the experimental data among the ab initio methods.

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