



Ab-initio complex molecular potential energy surfaces by the back-rotation transformation method

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ABSTRACT

The imaginary part of the complex potential energy surface (CPES) provides the autoionization, Auger and ICD (Intermolecular Coulombic Decay) ionization decay rates as functions of the variations in the molecular electronic structure and geometry. We introduce here a novel approach which enables the calculations the molecular *complex* potential energy surfaces by the standard computational algorithms which were originally developed for calculating *real* PES of stable molecules. As an illustrative numerical example we have calculated the CPES for the molecular autoionization of hydrogen molecule, $H_2[{}^1\Sigma_g^+]$ where the two electrons are doubly excited.

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1. Motivation and the problem

The recent developments in free-electron laser technology and synchrotron radiation sources provide the facilities needed to carry out experiments on electronic wave packet dynamics. Theoretical studies of electronic wave packet dynamics in molecules is a challenge mainly because of the need to include couplings between the electronic and nuclear coordinates into molecular wave packet propagation calculations. These couplings can have a dramatic effect on the molecular dynamics. Apart from this problem, it is also of interest to analyze within the adiabatic approximation the effect of molecular ionization as a function of nuclear coordinates. For example, it might happen that the motion of the electronic wave packet is accomplished via molecular ionization. The rate of ionization depends heavily on nuclear motions.

However, molecular propagation calculations where the electron–nuclei couplings (non adiabatic effects) are taken into consideration are very difficult, if not impossible, even with the most advanced computational facilities.

In order to include electronic ionization effects while the nuclei are moving (*within the adiabatic approximation*), the time-dependent Schrödinger equation must be solved with complex potential energy surfaces (CPES) [1–3].

The CPES are the complex eigenvalues of the electronic Born–Oppenheimer (BO) molecular Hamiltonian as functions of the nuclear positions, $\{\mathbf{R}_\alpha\}$. CPES are also obtained with complex absorbing potentials (CAPs) added to impose outgoing boundary

conditions [5]. In order to minimize the artificial reflection effects on the molecular dynamics which are due to the CAPs, the CAP parameters should be optimized. There are no universal problem independent CAPs. Hence calculating a reliable complex PES is still an open problem [6]. In principle we know that we need to solve the electronic time independent Schrödinger equation within the BO approximation with outgoing boundary conditions (so called Siegert boundary conditions) that describe the free-moving ionized electrons. Under outgoing boundary conditions the BO Hamiltonian has a discrete electronic spectrum, with real discrete eigenvalues associated with electronic bound states and complex discrete eigenvalues associated with metastable (resonance) electronic states, $E_n(\{\mathbf{R}_\alpha\})$, where $-2\text{Im}[E_n(\{\mathbf{R}_\alpha\})]$ is the ionization decay rate,

$$\begin{aligned} \hat{H}^{elec} \Psi_n^{elec}(\{\mathbf{r}_j\}_{j=1,\dots,N}, \{\mathbf{R}_\alpha\}_{\alpha=1,2,\dots}) &= E_n(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots}) \Psi_n^{elec}(\{\mathbf{r}_j\}_{j=1,\dots,N}, \{\mathbf{R}_\alpha\}_{\alpha=1,2,\dots}) \\ \lim_{|\mathbf{r}_j| \rightarrow \infty} \Psi_n^{elec}(\{\mathbf{r}_j\}_{j=1,\dots,N}, \{\mathbf{R}_\alpha\}_{\alpha=1,2,\dots}) &\rightarrow \infty \\ \hat{H}^{elec} &= T_e + V_{eN} + V_{ee} \end{aligned} \quad (1)$$

Here T_e , V_{eN} and V_{ee} are respectively, the electronic kinetic energy operator, electron–nuclei potential energy operator and the electronic repulsion energy operator. In Eq. (1) the wavefunction tends to infinity resulting from the requirement of outgoing boundary condition. This behavior results from the fact that the outgoing wavefunction behaves like $\exp(ikr)$ asymptotically. For bound states $k = i|k|$ and for resonances $k = |k|r^{-ix}$ such that $\exp(ikr) \rightarrow \infty$. By imposing outgoing (Siegert) boundary conditions a discrete spectra is obtained associated with bound (real eigenvalue) and resonance *complex eigenvalues) states.

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In the present work, we provide a method for calculating CPES which is based on two steps in the numerical calculations. In the first step of the calculations non-physical CPES are obtained by rotating the positions of all electrons and all nuclei in the molecule into the complex coordinate plane (complex scaling parameter). It is quite straightforward to do these type of calculations using standard widely used electronic structure packages since the Born–Oppenheimer molecular hamiltonian is dilation analytic only when the positions of electrons *and also* the nuclei are complex scaled. In the second step of the calculations the physical CPES are obtained by carrying out back-rotation transformation of the nuclei positions to the real physical axis.

The complex scaling transformation [7] has the advantage that it suppresses the asymptote exponential divergence of the resonance wavefunctions and makes them be square integrable and therefore standard computational algorithms originally developed for calculating real PES of stable molecules could be used. However, the complex scaling transformation is *not* applicable to the molecular Hamiltonian within the framework of the Born–Oppenheimer approximation since *the electron-nuclei attraction potential energy term is not dilation analytic* [8–10]. The attraction potential energy term between the j -th electron and the α -th nuclei is given by

$$V_{eN}(\mathbf{r}_j, \mathbf{R}_\alpha) = -\frac{Z_\alpha e^2}{|\mathbf{r}_j - \mathbf{R}_\alpha|} \quad (2)$$

It is implied that in the center-of-mass reference frame V_{eN} is an analytical function of the electronic coordinates (i.e., a Taylor series expansion for the electronic coordinates converges) only for the case where

$$|\mathbf{r}_{j=1,2,\dots}| < |\mathbf{R}_{\alpha=1,2,\dots}|. \quad (3)$$

In a case where the electron moves along the x -coordinate and the nuclear position is $(1, 0, 0)$, $V_{eN} = -\sqrt{[1/(1-x_e)]^2} = -\sqrt{[\sum_{n=0}^{\infty} x_e^n]^2}$ converges if and only if $x_e < 1$. Therefore if $x_e < 1$ (which is not a physical situation since $-\infty \leq x_e \leq +\infty$), then we can scale the electronic coordinate by $e^{i\theta}$ without scaling the nucleus, $V_{eN}(e^{i\theta}x_e, X_n = 1) = -\sqrt{[\sum_{n=0}^{\infty} x_e^n e^{in\theta}]^2}$. However, V_{en} is not an analytical function (i.e., the Taylor series expansion for the electronic coordinates does not converge) when $|\mathbf{r}_{j=1,2,\dots}| \geq |\mathbf{R}_{\alpha=1,2,\dots}|$. Therefore we cannot analytically continue the electronic coordinates over the entire space.

2. The solutions to the problem

2.1. The known solutions

Let us first mention the known solutions to the problem. By carrying out the exterior scaling transformations [11–13] the electronic coordinates are kept along the real axis and only when they are far from the nuclei positions where $V_{en} = 0$, are the electronic coordinates rotated into the complex plane. See for example the calculations of complex potential energy curves by using exterior complex scaling in Ref. [14]. Another similar solution is the smooth exterior scaling which has been shown to be equivalent to adding universal energy independent non-local complex non-Hermitian operators [15]. Yet another solution for diatomic molecules is the use of prolate spheroidal coordinates [16]. However, it is numerically difficult to apply these solutions to the problem of calculating molecular electronic complex potential surfaces. But, although it is indeed difficult to impose outgoing boundary conditions, it has been done. See, for example, the use of R -matrix for the calculations of the virtual state of CO_2 [17].

2.2. The new solution

The new solution to the problem which is briefly sketched in [18] enables one to calculate the bound and the resonance (not virtual) complex electronic potential energy surfaces by using the electronic structure codes which are available.

Here we first present the details of these numerical calculations. As the first step of the calculations *all the electronic and nuclear coordinates are complex scaled* and only then are the eigenvalues of the Born–Oppenheimer Hamiltonian computed. In the second step of the calculations a back transformation operation is carried out in order to obtain the desired CPES. It is obvious, however, that we can overcome the non-dilation analyticity by scaling not only the electronic coordinates but also the nuclear coordinates [19], such that,

$$V_{eN}(e^{i\theta}\mathbf{r}_j, e^{i\theta}\mathbf{R}_\alpha) = e^{-i\theta}V_{eN}(\mathbf{r}_j, \mathbf{R}_\alpha) \quad (4)$$

Therefore, based on the Balslev–Combes theorem [8–10] by scaling all electronic and nuclear coordinates by a complex factor $\exp(i\theta)$, the resonance PES is obtained for a non-physical situation where the nuclei positions are not on the real axis but rotated into the complex coordinate plane,

$$\begin{aligned} & [\hat{H}_\theta^{elec} - W_n^\theta(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N})] \Psi_n^{elec}(\{e^{i\theta}\mathbf{r}_j\}_{j=1,\dots,N}, \{e^{i\theta}\mathbf{R}_\alpha\}_{\alpha=1,2,\dots,N}) = 0 \\ & W_n^\theta(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}) = E_n(\{e^{i\theta}\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}) \\ & \lim_{|\mathbf{r}_j| \rightarrow \infty} \Psi_n^{elec}(\{e^{i\theta}\mathbf{r}_j\}_{j=1,\dots,N}, \{e^{i\theta}\mathbf{R}_\alpha\}_{\alpha=1,2,\dots,N}) \rightarrow 0 \\ & \hat{H}_\theta^{elec} = e^{-2i\theta}T_e + e^{-i\theta}V_{eN} + e^{-i\theta}V_{ee} \end{aligned} \quad (5)$$

There is no reason to look for complex stationary solutions for which $dW_n/d\theta = 0$ and no reason to assume that such stationary points exist. In fact, we expect W_n^θ to be an analytical function of $\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}$ that shows a monotonic behavior with the variation of the complex scaling parameter $\exp(i\theta)$. Hence in the second step of our calculations we carry out a back-rotation (BR) transformation to return the complex scaled positions of the molecular nuclei back to the real physical positions. There are different methods to carry out the back-rotation transformation. Let us mention as an example the Padé approach that has been used before by Lefebvre and his co-workers for calculating the resonance widths [20]. Another very simple and convenient procedure that we use here is the Taylor series expansion. By carrying out the Taylor series expansion of $W_n^\theta(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N})$ in $\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}$ and substitute $\mathbf{R}_\alpha^{BR} = e^{-i\theta}\mathbf{R}_\alpha$ in the Taylor series expansion of W_n then the desired result where

$$W_n^\theta(\{\mathbf{R}_\alpha^{BR}\}_{\alpha=1,\dots,N}) = E_n^{BR}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}, \theta). \quad (6)$$

is obtained.

The back-rotation transformation (BRT) is given by

$$\begin{aligned} E_n^{BR}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}, \theta) & \equiv W_n^\theta(\{\mathbf{R}_\alpha^{BR}\}_{\alpha=1,\dots,N}) \\ & = \sum_{j_1 j_2 \dots j_N} a_{j_1 \dots j_N} \prod_{\alpha=1}^N \left([\mathbf{R}_\alpha^{BR} - \mathbf{R}_\alpha]^{j_\alpha} \right) \end{aligned} \quad (7)$$

where

$$a_{j_1 \dots j_N} = \prod_{\alpha=1}^N \frac{1}{j_\alpha!} \partial_{\mathbf{R}_\alpha}^{j_\alpha} W_n^\theta(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}) \quad (8)$$

The Taylor series expansion in Eq. (7) is truncated to N_{Taylor} terms. The value of N_{Taylor} is chosen to get converged stationary CPES. Namely, the autoionizing or Auger or ICD resonance CPEC are obtained from the requirement of

$$\left[\nabla_{\theta, N_{Taylor}} E_n^{BR}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}, \theta, N_{Taylor}) \right]_{\theta_{opt}, N_{Taylor}^{opt}} = 0 \quad (9)$$

Note that the physical CPES obtained from the cusp in the θ and N_{Taylor} trajectory calculations. The method we develop here for calculating CPEC for molecular autoionizing, Auger or ICD resonance decaying processes is summarized in Eqs. (7)–(9).

In order to carry out wavepacket dynamics on CPES we need to add to $E_n(R)$ the nuclear–nuclear repulsive potential energy term

$$V_{NN}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}) = \sum_{\alpha' > \alpha} \frac{e^2 Z_{\alpha'} Z_\alpha}{|\mathbf{R}_{\alpha'} - \mathbf{R}_\alpha|} \quad (10)$$

Such that

$$E_n^{BR}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}, \theta, N_{Taylor}) \rightarrow E_n^{BR}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}, \theta, N_{Taylor}) + V_{NN}(\{\mathbf{R}_\alpha\}_{\alpha=1,\dots,N}). \quad (11)$$

In practice for polyatomic molecules we do not have $3N$ degrees of freedom in the calculations of potential surfaces (PES) but $3N-6$ where $N \geq 3$. The reduction in the number of degrees of freedom results from our requirement of three specific atoms to be in the X - Y plane. Namely, the nucleus of one of the atoms is held fixed at the origin, the nucleus of a second atom is placed on the X -axis, and the nucleus of the third atom is embedded in the X - Y plane. Moreover, the PES are described in terms of the internal degrees of freedom which consists of internuclear distances, angles, and dihedral angles. For diatomic molecule one nucleus is placed at the origin $(0,0,0)$ while the second nucleus at $(R,0,0)$. In such a case we need to carry out the back rotation transformation for the internuclear distance R only. Consequently, in the case of diatomic molecules Eq. (7) is replaced by the following equation,

$$E_n^{BR}(R, \theta, N_{Taylor}) = \sum_{j=0}^{N_{Taylor}} \left[\frac{R^j (e^{-i\theta} - 1)^j}{j!} \right] \left[\frac{\partial^j W_n^\theta}{\partial R^j} \right] \quad (12)$$

The value of N_{Taylor} and the optimal scaling angle θ are chosen to get a cusp in the θ and in N_{Taylor} trajectory calculations as described above in Eq. (9). This subject is discussed in some more detail in the next section.

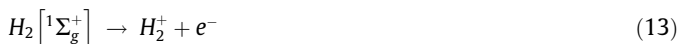
For a triatomic molecule we have two internuclear distances R_1 and R_2 and one angle (e.g., the position of one nucleus is at $(0,0,0)$ for any rotational angle θ , the second nucleus is placed at $(R_1 e^{i\theta}, 0, 0)$, and the third nucleus is placed at $(R_2 e^{i\theta} \cos \alpha, R_2 e^{i\theta} \sin \alpha, 0)$. In such a case the coefficients of the Taylor series expansion given in Eq. (8) are the derivatives of the complex electronic energy, which have been calculated by rotating the positions of the electrons and the nuclei into the complex coordinate plane, by the internuclear distances R_1 and R_2 . Namely, $R_1 \rightarrow R_1 e^{-i\theta}$ and $R_2 \rightarrow R_2 e^{-i\theta}$. Therefore, the n -th CPES for triatomic molecules can be denoted by $E_n^{BR}(R_1, R_2, \theta, \alpha, N_{Taylor})$. The optimal CPES is defined for the values of θ for which we have stationary solutions, i.e. $\partial E_n^{BR}(R_1, R_2, \theta, \alpha, N_{Taylor}) / \partial \theta|_{\theta_{opt}(R_1, R_2, \alpha)} = 0$. In a very similar way our approach for the back rotation transformation of the nuclei can be carried out for any polyatomic molecule.

There is a delicate point which we should mention here. Although the molecular Hamiltonian within the framework of the Born Oppenheimer Hamiltonian, $H(R)$, is not analytic, it is possible to construct an analytic family of operators that has the same spectrum as $H(R)$ and prove analyticity of the energy [21]. Therefore, although we can evaluate by our method the complex potential energy surfaces when the nuclei positions are on the real physical axis we cannot compute the resonance electronic wavefunctions. This is the main limitation of our approach. However, the resonance electronic wavefunctions can be computed by rotating backward both the electronic and the nuclei resonance wavefunctions to the real axis. Of course the rotating backward transformation of the resonance wavefunction can be carried out only after applying our approach which provides the resonance complex eigenvalue, the optimal complex scaling angle θ , and enables us to identify the res-

onance wavefunction. The resonance wavefunction which is obtained after applying the backward rotational transformation is not in the Hilbert space and its asymptote diverges exponentially. Yet, by applying one of the methods mentioned above (such as exterior scaling) the resonance wavefunction becomes square integrable.

3. Testing the novel computational procedure

We will test the method described above for the calculations of the complex potential energy curve (CPEC) for the autoionizing resonance state of $H_2[{}^1\Sigma_g^+]$ where the two electrons are excited. The autoionization process is given by,



where H_2^+ is its ground electronic state. The CPEC of the autoionizing hydrogen molecule are calculated with the full configuration interaction (FCI) method. An atom centered NASA Ames ANO basis set [22] augmented with three sets of the even-tempered Gaussian basis functions has been employed for FCI calculation. The exponents of the even-tempered basis functions are calculated using

$$\zeta_i^{S/P} = (\zeta^S/P)^{(1/N^{S/P})} \zeta_{i-1}^{S/P}, \quad (14)$$

where the parameters for the three even-tempered sets of functions are as follows:

1. $\zeta_0^S = 50, \zeta^S = 0.0001, N^S = 10$ (centered on each atom)
2. $\zeta_0^P = 5, \zeta^P = 0.005, N^P = 4$ (centered on each atom)
3. $\zeta_0^S = 5, \zeta^S = 0.005, N^S = 5$ (positioned on both sides of the molecular axis and centered at 2 and 3.5 a.u. away from the molecular centre).

The non-physical $W^\theta(R)$ is the complex energy which is a function of the internuclear distance, R , and the complex scaling angle θ which were obtained from our ab initio calculations when the electronic coordinates and also R were scaled by a complex factor $e^{i\theta}$. At $R = 0$ the electronic energy (in the absence of the nuclear repulsion $4/R$) the eigenfunction of $H_2[{}^1\Sigma_g^+](R=0)$ is exactly the resonance complex eigenvalue of the auto-ionization of doubly electronically excited helium atom $He(2s)^2 \rightarrow He^+ + e^-$. Therefore in our FCI calculations we followed adiabatically the known complex scaled resonance function of $He(2s)^2$ as R has been varied and obtained $W^\theta(R)$ for different values of θ . This is the first step of the numerical calculations of CPEC of $H_2[{}^1\Sigma_g^+](R)$ as it has been described above in the section where we described our solution to the problem of calculating CPEC by complex scaling.

In the second step of our procedure for calculating CPES of $H_2[{}^1\Sigma_g^+](R)$ we obtained the desired CPEC by carrying out the BRT as defined in Eq. (12). The physical CPEC of $H_2[{}^1\Sigma_g^+](R)$ is defined as

$$E(R^{BR}, \theta, N_{Taylor}) = E_r(R, \theta, N_{Taylor}) - i/2\Gamma(R, \theta, N_{Taylor}) \quad (15)$$

(where E_r is the resonance position and Γ is the resonance width which that is inverse proportional to the decay rate of the metastable resonance state) when θ and N_{Taylor} parameters are optimized to get a cusp behavior in the θ and N_{Taylor} trajectory calculations at which the two stationary conditions are satisfied,

$$\left[\frac{\partial E(R^{BR}, \theta, N_{Taylor})}{\partial \theta} \right]_{\theta_{opt}, N_{Taylor}^{opt}} = 0 \quad (16)$$

and

$$\left[\frac{\partial E(R^{BR}, \theta, N_{Taylor})}{\partial N_{Taylor}} \right]_{\theta_{opt}, N_{Taylor}^{opt}} = 0. \quad (17)$$

Let us first describe the results obtained by our method for the autoionization of $H_2\Sigma_g^+(\sigma_u^2)$ at $R = 1.4$ au) for which there are available results in the literature which were calculated by other methods.

3.1. Numerical results for the position and width of the autoionization resonance of $H_2[{}^1\Sigma_g^+](R = 1.4$ a.u.)

The results presented in Figure 1 clearly show how the rate of autoionization of doubly electronically excited hydrogen molecule is calculated by the back-rotation method (BRT) for the internuclear distance, $R = 1.4$ a.u. The cusp obtained for back rotated complex potential energy curve of doubly electronically excited H_2 molecule which is shown in Figure 1 is when we have used only two terms in the Taylor series expansion given in Eq. (12) (i.e., $N_{Taylor} = 2$). The fact that the stable cusp is obtained for $N_{Taylor} = 2$ is shown in Figure 1. In Figure 2 we plotted the results obtained from θ -trajectory calculations where $N_{Taylor} = 1, 2, 3$. It is clear that there is no cusp when only one term in the Taylor expansion is included. However, we see from the results presented in Figure 2 that the cusp obtained for $N_{Taylor} = 2$ is exactly as for $N_{Taylor} = 3$ (within the numerical accuracy shown in Figure 3). There slightly deviations of location of the cusp in the complex energy plane when $N_{Taylor} \gg 2$ are expected since we have used in our numerical calculations of the derivatives only seven grid points of R . The number of the grid points of R we have used for calculating the derivative terms in the Taylor expansion determines the value of N_{Taylor} for which a stable cusp in the complex energy plane is obtained. Using the optimal values for the scaling angle θ and for the number of terms in the Taylor series expansion, N_{Taylor} the two conditions given in Eq. (9) were satisfied. Using the optimal values of θ and N_{Taylor} we obtained the results which are presented in Table 1 and are compared with the results obtained by other methods for H_2 doubly electronic excited state at $R = 1.4$ a.u.

The convergence of the procedure of back rotation has been effected through a stabilization with respect to the two parameters: the complex scaling parameter θ and N_{Taylor} which is the number of

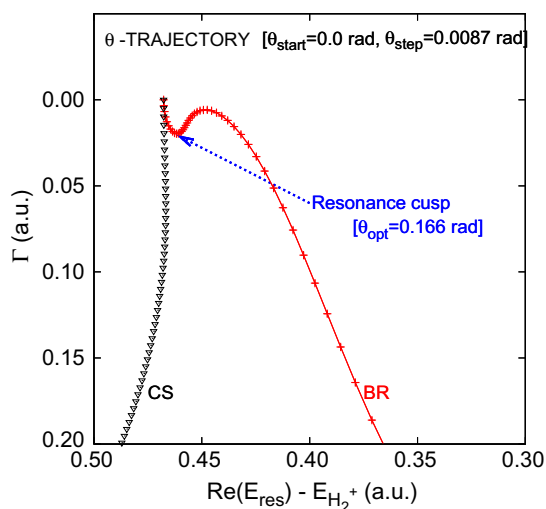


Figure 1. θ -trajectory calculations for a doubly excited hydrogen molecule, $H_2\Sigma_g^+(\sigma_u^2)$, as obtained from a complex scaling calculations (CS) where the internuclear distance R is rotated into the complex plane, $W^\theta(R = 1.4$ a.u.), and the θ -trajectory as obtained after applying the back-rotation transformation (BRT) to return R into the physical real axis, $E(R = 1.4$ a.u.) (see Eq. (12) in the text). Using the BRT method a cusp is obtained as expected (see Eq. (9) in the text) while $W^\theta(R = 1.4$ a.u.) does not support any stationary solution in the θ -trajectory calculations. The real part of the θ -trajectory is shifted with respect to the threshold energy which is the ground state of H_2^+ .

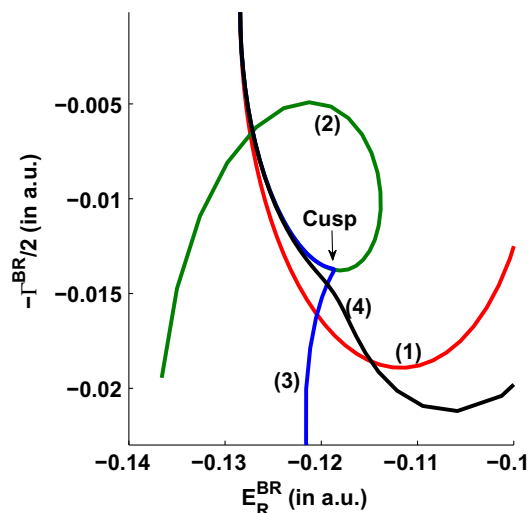


Figure 2. The complex energies of doubly excited hydrogen molecule, $H_2\Sigma_g^+$, as obtained from the θ -trajectory calculations are presented for different number of terms in the Taylor series expansion, N_{Taylor} , which are used in the back-rotation (BR) transformation (see Eq. (12)). The stable cusp condition is obtained here for $N_{Taylor} = 2$ (when the derivative terms in the Taylor series expansion were calculated by using seven grid points for $R = 1.4$ a.u.).

terms in the Taylor series. The number of terms in the series Taylor expansion for R which are needed to get converged results depends of the smoothness (i.e., curvature) of the function $E^{el}(R)$. Usually the curves are smooth functions of R and therefore it is expected to get a convergence of the Taylor series expansion for small values of R and in particular since the deviation of $\exp(i\theta)$ from 1 is small. Indeed in our numerical calculations we get a convergence for $N_{Taylor} = 2, 3, 4$. However, for more complicated situations such as for a PES that includes conical intersections our approach is not expected to be applicable.

3.2. Numerical results for the autoionizing resonance CPEC of $H_2[{}^1\Sigma_g^+](R)$

By repeating on the two steps in our numerical calculations as described above we have obtained the autoionizing resonance CPEC of $H_2[{}^1\Sigma_g^+](R)$. We concentrate here on the doubly excited state that is above the threshold of ionization. In this particular case it is expected that the united atom limit is the $1S^e$ doubly excited state of Helium with energy -0.777868 and lifetime of 0.004541 a.u. In our calculations we could not carry out calculations in the limit of $R \rightarrow 0$ since several avoided crossings exist as $R \rightarrow 0$ (united atom). The back rotation transformation based on the Taylor series expansion presented in this Letter is applicable for the situations where we do not have many overlapping avoided crossings. In Figure 3 the resonance energy position and width of $H_2[{}^1\Sigma_g^+](R)$ as function of R are presented. Our results show that with increasing the internuclear distance the autoionization molecular resonance approaches the threshold energy (the ground state energy of the H_2^+ molecular ion). The resonance position of electronically excited hydrogen molecule 'hits' the threshold energy at $R \approx 2.4$ a.u. This is in comparison of $R \approx 2.7$ a.u. obtained before by using the exterior scaling procedure [14] and of $R \approx 2.8$ a.u. by using the Feshbach theory and an L^2 representation of the non resonant continuum with B-spline functions [26]. The differences between the values of R at which the resonance 'hits' the threshold energy which were obtained from the different type of computational approaches are due to the difficulty in studying the resonance to bound transition as R is varied by using square integrable basis functions. The question whether there is a true

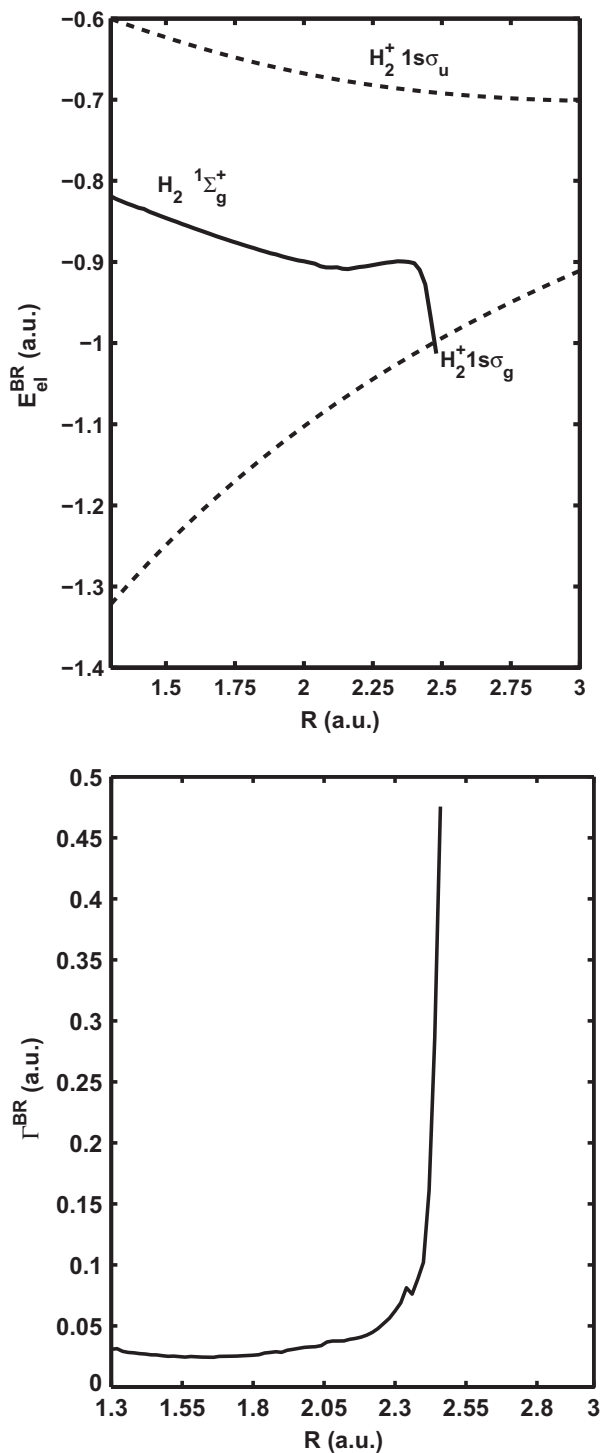


Figure 3. The complex energy curve (including the nuclear repulsion) of doubly excited hydrogen molecule, $H_2^+ 1s\sigma_g^+$, as obtained from the back-rotation (BR) transformation (see Eq. (12)) where the cusp condition given in Eq. (9) is satisfied for any internuclear distance R . (a) The real part of the complex energy values which provide the resonance energy position as function of R (b) The imaginary part of the complex energy values which provide the resonance energy width as function of R . Note that for $R = 2.4$ a.u. the resonance state ‘hits’ the threshold energy which is the ground state of H_2^+ .

bound state at the threshold or there is no bound state at the threshold has been discussed many years ago by Klaus and Simon [27] (see also Ref. [28] and references therein). In the first case the Hellman–Feynman theorem implies that the eigenvalue hits the continuum linearly in R (the relevant potential parameter in our

Table 1
Energy and width of the lowest $1\Sigma_g^+$ Feshbach resonance in H_2 at the internuclear distance $R = 1.4$ a.u.

Method	$[\Re E_{res} - E_{H_2^+}]$ (a.u.)	Γ (a.u.)
CI (NM&CC) [4]	0.4726	0.0445
Projection operator [23]	0.4667	0.0254
SEP R matrix [24]	0.4740	0.0276
RF-CAP [25]	0.4615	0.0227
CR-CAP [6]	0.4648	0.0178
This work	0.4618	0.0197

case) and a ‘first-order phase transition’ in the plot of resonance width vs. its position as R is varied will be observed. However, if there is *no* bound state at the threshold, then the eigenvalue merges into the continuum as the potential parameter (R in our case) is varied, i.e., a ‘second-order phase transition’ will be observed. This behavior occurs in many atomic systems [28] and also in our case as our results presented in Figure 3b show. Our results shown in Figure 3 that the resonance width is increased as the resonance position approaches the threshold energy results from the fact that the $H_2[1\Sigma_g^+](R)$ is a Feshbach type resonance. Feshbach type resonances are often described within the framework of the ‘zero-order’ approximation as bound states in the continuum. The decay process is associated with the coupling between the so called bound states with the continuum. As this coupling becomes stronger the rate of decay is larger (i.e., larger width). Since the density of states in the continuum in our case is linearly proportional to the square root of the inverse of the energy gap between the resonance position and the threshold energy of H_2^+ it is clear that the behavior of $\Gamma(R)$ as R is varied should be as it has been obtained from our numerical calculations.

4. Conclusions

The back-rotation method is based on the Balslev–Combes proof that the complex scaling method is applicable for dilation analytic Hamiltonians. Therefore we scale both the electronic and the nuclear coordinates within the framework of the Born–Oppenheimer (BO) approximation since only then the BO Hamiltonian is dilation analytic and all terms are homogeneous functions of the scaling parameter. The problem is that the complex eigenvalues of the complex scaled adiabatic (i.e., BO) Hamiltonian are for a non-physical geometrical structure of the molecule where the nuclear positions are rotated into the upper complex coordinate plane. To overcome this problem we carry out a back-rotation transformation to bring back the nuclear positions into the real physical plane. We have tested this method for calculating complex potential energy surfaces (CPES) for calculating the complex potential energy curve of autoionizing hydrogen molecule. It is straight forward to apply our method to many electron polyatomic molecules by using standard computational algorithms which originally were developed for calculating real PES of stable molecules.

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