A study of complex scaling transformation using the Wigner representation of wavefunctions

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The complex scaling operator \( \exp(-\theta \hat{\partial} / \hbar) \), being a foundation of the complex scaling method for resonances, is studied in the Wigner phase-space representation. It is shown that the complex scaling operator behaves similarly to the squeezing operator, rotating and amplifying Wigner quasi-probability distributions of the respective wavefunctions. It is disclosed that the distorting effect of the complex scaling transformation is correlated with increased numerical errors of computed resonance energies and widths. The behavior of the numerical error is demonstrated for a computation of CO\(^{2+}\) vibronic resonances. © 2011 American Institute of Physics. [doi:10.1063/1.3583816]

I. INTRODUCTION

The complex scaling method\(^{1-4}\) is one of the few methods for calculating the resonances (or Siegert states), i.e., quantum states that are not part of the hermitian spectrum of Hamiltonian.\(^5\) Among the alternative methods mention the smooth exterior complex scaling\(^6-9\) and the complex absorbing potential.\(^10,11\) All the methods are closely related, where the smooth exterior complex scaling is actually a more general version of the complex scaling, while the complex absorbing potential, although originating in quantum dynamics,\(^12\) has proven to be an approximation to the smooth exterior complex scaling.\(^13-17\) Considerable attention was paid to the application of these methods for calculations of electronic resonances, where many studies were devoted to the development of methodology,\(^18-22\) while others were devoted to specific applications, such as autoionization,\(^7,25-28\) interatomic Coulomb decay,\(^29-32\) decay of temporary anions,\(^33-38\) or multiphoton processes.\(^39-54\) The methods for direct calculation of resonances were further applied to study vibronic processes, such as photodissociation of molecules in van der Waals clusters,\(^55-58\) predissociation due to conical intersections,\(^59,60\) predissociation of dications,\(^61-63\) and others.\(^64-69\) Debated methods found their use in the scattering problem as well, where Refs. 70–72 deal with the formulation of general theory, while other studies deal with its applications for the gas\(^73-77\) and surface scattering.\(^78-82\) Furthermore, these methods have been applied to study Bose-Einstein condensates,\(^83,84\) quantum dots,\(^85\) resonant tunneling in molecular junctions,\(^86,87\) and others. Earlier review articles as well as a recently published monograph dedicated to the theory of resonances can be found in Refs. 88–90.

The complex scaling method is based on the complex scaling transformation of wavefunctions and operators, where the physical Hamiltonian \( \hat{H} \) is replaced by the transformed one, \( \hat{H}_\theta \), which is given by

\[
\hat{H}_\theta = \hat{S}_\theta \hat{H} \hat{S}_\theta^{-1},
\]

where \( \hat{S}_\theta \) is the complex scaling operator given by

\[
\hat{S}_\theta = e^{-\theta \hat{\partial} / \hbar}, \quad \theta \in \mathbb{R}, \quad 0 \leq \theta < \pi / 4.
\]

The Hamiltonian transformation implies that physical wavefunctions \( f(x) \) are replaced by the complex scaled ones \( f_\theta(x) \), where \( f_\theta(x) = f(x e^{i\theta}) \). The complex scaling transformation dampens diverging outgoing parts of wavefunctions, which define Siegert eigen-states of Hamiltonian (resonances) in coordinate representation. The transformed resonance wavefunctions are square integrable and therefore convenient for computational approaches.

This paper represents a free follow-up on an idea of using the Wigner phase-space formulation of quantum mechanics to study complex scaling, first used in Ref. 91. The present study is focused on the effect of the complex scaling transformation on a resonance wavefunction. We show that the complex scaling operator behaves similarly to the squeezing operator, rotating and amplifying Wigner quasi-probability distributions of the respective wavefunctions. It is disclosed that the distorting effect of the complex scaling transformation is correlated with increased numerical errors of computed resonance energies and widths. The behavior of the numerical error is demonstrated for a computation of CO\(^{2+}\) vibronic resonances. © 2011 American Institute of Physics. [doi:10.1063/1.3583816]
the scalar product of two transformed Wigner distributions, where, however, each one of them is given by a mirror image of the other one in respect to the $p$-axis. As the complex scaling parameter $\theta$ is increased, the overlap of the two distributions happens to decrease lowering the computational precision of the complex scaling method.

This paper is organized as follows: In Sec. II, we derive a transformation $\hat{Z}_\theta$, which is a counterpart of the complex scaling operator $\hat{S}_\theta$, defined for Wigner distributions, and discuss its effect using simple examples. In Sec. III, we deal with a formulation of the generalized scalar product using the Wigner phase-space representation and an exact estimation of a computational error for complex resonance energies obtained via the complex scaling method. Finally, in Sec. IV, we present an example application of the complex scaling method for CO$^{2+}$ predissociation resonances, where we illustrate the specific behavior of the numerical error of the computed resonance energies, caused by using the complex scaling transformation. In Sec. V we provide a summary of the present study and its conclusions.

II. A PHASE-SPACE EQUIVALENT TO THE COMPLEX SCALING OPERATOR

The theory of Wigner phase-space representation of quantum mechanics was developed in the fundamental works $^{92-95}$ and later became the subject of many review articles, such as Refs. $^{96-98}$. It defines the one-to-one mapping of wavefunctions $f(x)$ onto quasi-probability Wigner distributions $\tilde{f}(x, p)$ according to the following formula:

$$\tilde{f}(x, p) = \text{tr}[\hat{f}] \langle f | \hat{w}(x, p) \rangle,$$

where $|f\rangle$ is the state vector corresponding to the wavefunction $f(x)$ and $\hat{w}(x, p)$ represents the Weyl operator given by

$$\hat{w}(x, p) = \int_{-\infty}^{\infty} d\Delta x \left( x + \frac{\Delta x}{2} \right) e^{ip\Delta x/\hbar} \left( x - \frac{\Delta x}{2} \right)\right),$$

where $\Delta x = x + p$, ensures that $\hat{S}_\theta$ always operate on integrable functions from the left. This allows us to use the identity $\hat{S}_\theta = e^{i\theta} \hat{S}_\theta$, which follows from the commutation relation $[\hat{x}, \hat{p}] = i\hbar$, such that

$$\hat{w}_\theta(x, p) = e^{i\theta} \hat{S}_\theta \hat{w}(x, p) \hat{S}_\theta.$$

The right hand side of Eq. (8) can be expressed by the phase-space integral,

$$\tilde{f}_\theta(x, p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx' dp' \tilde{f}(x', p') \tilde{w}_\theta(x', p'; x, p),$$

where $\tilde{w}_\theta(x', p'; x, p)$ is defined as the Wigner transform of the Weyl operator $\hat{w}_\theta(x, p)$ given by,

$$\tilde{w}_\theta(x', p'; x, p) = \langle \hat{x}, \hat{p} \rangle \tilde{w}_\theta(x', p') \hat{S}_\theta \hat{w}(x, p) \hat{S}_\theta.$$

By a direct substitution for the Weyl operators $\tilde{w}(x', p')$ and $\hat{w}(x, p)$ [Eq. (6)], we obtain

$$\tilde{w}_\theta(x', p'; x, p) = e^{i\theta} \langle \hat{x}, \hat{p} \rangle \tilde{w}(x', p') \hat{S}_\theta \tilde{w}(x, p) \hat{S}_\theta.$$

Next we express the matrix elements that we get from these definition formulas, $\langle x | \hat{S}_\theta | p \rangle = \exp(i x e^{i\theta} \rho/\hbar)$ and
(p|\tilde{S}_0| x) = e^{-i\theta} \exp(-ixp e^{-i\theta}/\hbar) \tilde{w}_0(x', p'; x, p) = (2\pi\hbar)^{-1} e^{-2px^* \sin \theta / \hbar} 
\times \int_{-\infty}^{\infty} d\Delta_n^* d\Delta_e^p e^{i\Delta_n^*(p' - p\cos \theta)/\hbar} 
\times e^{i\Delta_e^p(x' \cos \theta - x)/\hbar} e^{i\Delta_e^p \sin \theta / 2\hbar}. \quad (14)

The final term in Eq. (14) is expanded in Taylor series so as to enable a separation of the two integration variables such that

\[ e^{\Delta_e^p \sin \theta / 2\hbar} = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\sin \theta}{2\hbar} \right)^n \Delta_e^p \Delta_x^n. \quad (15) \]

Analytical integration, followed by a number of algebraic adjustments specified in the Appendix, eventually leads to

\[ \tilde{w}_0(x', p'; x, p) = \frac{2\pi \hbar}{|\cos \theta|} e^{-2px^* \tan \theta / \hbar} \times \sum_{m=0}^{\infty} \left( \frac{\hbar \tan \theta}{2} \right)^m \frac{1}{m!} \times \delta^{(m)}(x' - x \cos^{-1} \theta) \delta^{(m)}(p' - p \cos^{-1} \theta), \quad (16) \]

where \( \delta^{(m)} \) denotes the \( m \)-th derivative of the Dirac \( \delta \)-function.

Finally, we substitute the function \( \tilde{w}_0(x', p'; x, p) \) into Eq. (11), thus obtaining the searched operator \( \tilde{Z}_0 \),

\[ f_0(x \cos \theta, p \cos \theta) = \frac{1}{|\cos \theta|} \tilde{Z}_0 f(x, p), \]

\[ \tilde{Z}_0 = e^{-(\sin \theta / \hbar) x p} e^{-(\tan \theta / 2\hbar) \hat{\eta}}, \quad (17) \]

where \( \hat{\xi}, \hat{\eta} \) are defined as

\[ \hat{\xi} = -i\hbar \frac{\partial}{\partial p}, \quad \hat{\eta} = i\hbar \frac{\partial}{\partial x}. \quad (18) \]

Allow us here to illustrate the application of \( \tilde{Z}_0 \) on the wavefunction \( f(x) \) given by the superposition of two minimum uncertainty Gaussians

\[ f(x) = f_1(x) + f_2(x), \]

\[ f_1(x) = e^{-x^2/2\hbar}, \]

\[ f_2(x) = e^{-(x-x_0)^2 / 2\hbar + ip_0 x / \hbar}, \quad (19) \]

where \( x_0 = 10 a_0 \) and \( p_0 = 4 a_0 \). The corresponding Wigner distribution \( \tilde{f}(x, p) \) is illustrated in Fig. 1 (the upper left panel). It includes two Gaussian auto-terms \( \tilde{f}_1 \) and \( \tilde{f}_2 \) corresponding to Wigner distributions of the individual Gaussians. The auto-terms have a probabilistic interpretation. An oscillatory cross-term \( (\tilde{f}_1, c.c.) \) appears between the auto-terms \( \tilde{f}_1, \tilde{f}_2 \). The cross-term is defined using the Weyl transformation of the cross-density matrix operator \( (\tilde{f}_1)(\tilde{f}_2) + c.c. \) such that

\[ \tilde{f}_{1,2}(x, p) = \text{tr}[\tilde{f}_1(\tilde{f}_2)]\tilde{w}(x, p). \quad (20) \]

Although the cross-term is “non-physical” in the sense of probabilistic interpretation, it defines the relative phase between the auto-terms. The phase-space transformation \( \tilde{Z}_0 \) is represented by a sequential action of the two operators such that \( \tilde{Z}_0 = \tilde{Z}_0^1 \tilde{Z}_0^q \), where

\[ \tilde{Z}_0^1 = e^{-(\sin \theta / \hbar) x p}, \quad \tilde{Z}_0^q = e^{-(\tan \theta / 2\hbar) \hat{\eta}}. \quad (21) \]
has a particular influence on the cross-term. The typical oscillatory behavior of the cross-term implies that \( \tilde{f}_{1,2} \) and \( \tilde{f}_{3,4} \) appear far from the center of the coordinate axes \([\eta, \xi]\) in the reciprocal Wigner space (the upper right panel in Fig. 1). Consequently, \( \tilde{f}_{1,2} \) and \( \tilde{f}_{3,4} \) are greatly influenced by the exponential multiplication due to the operator \( \tilde{Z}_0^{q} \) (the central right panel in Fig. 1). Unlike the cross-term, the auto-terms which have a typical non-oscillatory behavior are located in the center of coordinate axes \([\eta, \xi]\) in the reciprocal Wigner space. Therefore, \( \tilde{f}_1 \) and \( \tilde{f}_2 \) are slightly influenced by the operator \( \tilde{Z}_0^{q} \). The preferential action of the first operator, \( \tilde{Z}_0^{\tilde{q}} \), on the cross-terms, rather than auto-terms, is also apparent after a backward transformation of the modified distribution to the usual Wigner space \([x, p]\) (the central left panel in Fig. 1).

The second operator, \( \tilde{Z}_0^{q} \), is responsible for a modification of the auto-terms and a final modification of the cross-terms (the lower left panel in Fig. 1). This operator leads to a strong depletion of the probability in the first and fourth quarters (the auto-term \( \tilde{f}_2 \) has almost disappeared after complex scaling) and strong enhancement in the second and fourth quarters. The major influence of complex scaling on wavefunctions is evidently caused by the scalar operator \( \tilde{Z}_0^{\tilde{q}} \).

In another example, allow us to consider a wavefunction, which is defined as a sum of five Gaussian wavefunctions such that

\[
f(x) = \sum_{k=1}^{5} e^{-i(x-x_k)^2/2\hbar},
\]

where \( x_k = (-25 + 7.5 \cdot k) \) in the units of \( a_0 \). The Wigner distribution \( \tilde{f}(x, p) \) corresponding to \( f(x) \) is illustrated in the top panel in Fig. 2. \( \tilde{f}(x, p) \) is given by a superposition of five auto-terms associated with the individual Gaussians \( \tilde{f}_1, \ldots, \tilde{f}_5 \) and their cross-terms (\( \text{Re} \tilde{f}_{1,2}, \ldots, \text{Re} \tilde{f}_{4,5} \)). Figure 2 also shows the projections of \( \tilde{f}(x, p) \) onto the \( x \) and \( p \) axes, defining the probabilities \( |f(x)|^2 \) and \( |\langle p | f \rangle|^2 \), respectively.

The effect of the complex scaling operator \( \tilde{Z}_0^{q} \) is depicted in the middle panel in Fig. 2. \( \tilde{Z}_0^{q} \) causes an enhancement of the cross-terms, whereas the auto-terms remain nearly unchanged. The subsequent operator \( \tilde{Z}_0^{\tilde{q}} \) causes an effective rotation of the phase-space distribution with respect to the coordinate axes by the angle of \(-\theta\) (the bottom panel in Fig. 2) while the amplitudes of the auto-terms are strongly redistributed.

Finally, allow us to show how the two operators, \( \tilde{Z}_0^{q} \) and \( \tilde{Z}_0^{\tilde{q}} \), act on a metastable state. For this illustration, we choose an isolated shape resonance arising in the potential, which consists of a Morse oscillator and a potential barrier, which is added just before the start of the dissociation limit,

\[
V(x) = D_1(1 - e^{-ax})^2 - D_1 + D_2 e^{-i(x-x_0)^2/2\sigma^2}.
\]

The potential parameters are: for the Morse oscillator, the depth \( D_1 = E_h \), and the parameter \( \alpha = 0.5 a_0^{-1} \); for the potential barrier, the height \( D_2 = E_h \), the offset \( x_0 = 4 a_0 \), and the width \( \sigma = \sqrt{2} a_0 \). The mass of the particle is chosen as \( \mu = 10 \) \( m_e \). This potential well with the total depth of \( 2 E_h \) supports seven bound states and tunneling resonances. The highest lying one, characterized by the energy of \( 0.7126 \) \( E_h \) above the dissociation limit and the width of \( 0.0068 \) \( E_h \), be our example.

The coveted illustration first requires obtaining the unscaled resonance Wigner distribution \( \tilde{f}(x, p) \). Therefore it is necessary to calculate the unscaled resonance wavefunction \( f(x) \) on a sufficiently dense and long grid allowing for a numerical transformation into the Wigner representation. We addressed this issue using a quantum dynamical propagation, which simulates the collision process where the incident particle is composed of an extremely broad wavepacket, whose width exceeds the width of the numerical lattice several times. The dynamical system is controlled by the specific modulation of the giant incident wavepacket, so as to finally settle in the desired quantum state on the complex plane. The details of the construction of the giant incident wavepacket are given in our previous work, where we used this method to obtain unscaled wavefunctions of various complex Hamiltonian solutions for the first time.91

The Wigner distribution of the resonance wavefunction so obtained is shown in Fig. 3. The part of this distribution, which is characterized by concentric formations located in the interval of \(-1 a_0 > x > 4 a_0 \), resembles a distribution of a vibrational wavefunction, up to the fact that the regular rings are disrupted by the tunneling through the potential barrier. The outermost ring portrays the orbital motion of the classical particle, with the energy corresponding to the debated quantum wavefunction.
localized around the asymptotic region, where it is closely related to the shape resonance. We observe that the additional effect \( \hat{\theta} \) has caused an almost complete suppression of the outgoing probability distribution. The remaining distribution remains completely intact due to the effect \( \hat{Z}_\theta^{cl} \). The changes are noticeable in the area of the potential barrier, where the vibrational distribution is amplified for the negative momentum and reduced for the positive momentum.

The right column of Fig. 4 illustrates another case, which frequently occurs in the calculation of vibrational resonances, namely, that the bottom of the potential well is displaced from the beginning of the coordinate axis \( x \) and thus also from the center of complex scaling. The offset of the potential, here given by \( 5 \, a_0 \), causes a respective shift of the original Wigner distribution, \( f(x, p) \rightarrow f(x - 5, p) \). The top right panel demonstrates the fact, that the shift of the original Wigner distribution does not affect the outcome of the \( \hat{Z}_\theta^{cl} \) operator. On the other hand, the bottom right panel shows that the effect of the \( \hat{Z}_\theta^{cl} \) operator depends on the shift of the original Wigner distribution substantially. While in the case (i) the application of \( \hat{Z}_\theta^{cl} \) resulted in a distortion of the vibrational auto-term, so here in the case (ii), we can speak even of a “rotation” of the vibrational auto-term into the fourth quadrant. Unfortunately we cannot determine the angle of this rotation, as in the previous example, due to the fact that \( \theta \) is relatively small, \( \theta = 0.03 \), while the Wigner distribution of the seventh vibrational state exhibits much more complex structure than the Gaussians.

III. NUMERICAL ERROR OF VARIATIONAL ENERGIES OBTAINED USING THE COMPLEX SCALING METHOD

A. A view on the generalized inner product using the Wigner phase-space representation

The variational Ritz method combined with complex scaling transformation (known as the complex scaling method) represents the most common approach for computation of resonances. This method applies the variational principle to optimize complex energy expectation values \( \epsilon_{\theta} \), which are defined as

\[
\epsilon_{\theta} = \frac{\int dx \, f_\theta^{(l)}(x) \hat{H}_\theta \, f_\theta(x)}{\int dx \, f_\theta^{(l)}(x) f_\theta(x)},
\]

where \( \hat{H}_\theta \) is the complex scaled Hamiltonian Eq. (1). The searched wavefunctions \( f_\theta(x) \), \( f_\theta^{(l)}(x) \) are expanded in the basis sets \( \chi_l(x) \) and \( \chi^*_l(x) \), respectively, such that

\[
f_\theta(x) = \sum_{k=1}^{N} \chi_k(x) c_k,
\]

\[
f_\theta^{(l)}(x) = \sum_{k=1}^{N} \chi^*_k(x) c^{(l)}_k,
\]

and the variational principle is applied to find the coefficients \( c_k \) and \( c^{(l)}_k \). Then, the wavefunctions \( f_\theta(x) \) and \( f_\theta^{(l)}(x) \) represent the variational approximations to the eigenstates of the operators \( \hat{H}_\theta \) and \( \hat{H}_\theta^{(l)} \), respectively.

Now, we transform the definition of the computed energies \( \epsilon_{\theta} \), Eq. (24), using the Wigner phase-space formalism. First, we rewrite Eq. (24) using the density matrix formalism such that

\[
\epsilon_{\theta} = \text{tr} \left| f_\theta^{(l)} \right\rangle \left\langle f_\theta^{(l)} \right| \hat{H}_\theta \left| f_\theta \right\rangle \left\langle f_\theta \right|.
\]

Then, we replace the traces of the quantum operators by phase-space integrals using the appropriate rules for this transformation, which are described in Ref. 98, and obtain

\[
\epsilon_{\theta} = \frac{\int\int_{-\infty}^{\infty} dx \, dp \, f_\theta^{(l)}(x, -p) \hat{H}_\theta \, f_\theta(x, p)}{\int\int_{-\infty}^{\infty} dx \, dp \, f_\theta^{(l)}(x, -p)}.
\]
where $f_\theta^{(l)}(x, p)$ is defined as the Wigner distribution of the “left solution” $f_\theta^{(l)}(x)$ [Eq. (25)]. The phase-space operator $\hat{H}_\theta$ corresponding to $H_\theta$ is defined as

$$\hat{H}_\theta = V[e^{i\theta}(x + \xi/2)] + T[e^{-i\theta}(p + \eta/2)],$$

(28)

where the operators $\xi$ and $\eta$ are defined in Eq. (18).

Equation (27) shows that the generalized inner product corresponds to the scalar product of the Wigner distributions $\hat{f}_\theta(x, p)$ and $\hat{f}_\theta^{(l)}(x, -p)$ on the Wigner phase-space. In the case of resonances, which we are interested in, and bound states as well, the left and “right” solutions are equal, $f_\theta^{(l)}(x) = f_\theta(x)$, therefore the formula for resonance and bound-state energies is simplified such that

$$\epsilon_\theta = \frac{\iint_{-\infty}^{\infty} dx dp \ f_\theta(x, -p)\hat{H}_\theta f_\theta(x, p)}{\iint_{-\infty}^{\infty} dx dp \ f_\theta(x, -p)\ f_\theta(x, p)}.$$  

(29)

Here we see, that the generalized inner product corresponds to the scalar product of $\hat{f}_\theta(x, p)$ and its mirror image $\hat{f}_\theta(x, -p)$. The complex scaling transformation, which causes a phase-space rotation of the solutions $f_\theta(x, p)$, is compensated by multiplication with the left solutions $\hat{f}_\theta(x, -p)$, which are rotated exactly in the opposite direction. As a result of this compensation, the corresponding complex energies are calculated by a quantum averaging over the physically occupied phase-space regions, independent of the arbitrary complex scaling parameter $\theta$.

We may also observe, that the exponential outgoing parts of resonances are excluded from the quantum averaging based on the generalized inner product. The outgoing particle is represented by exponential tails of the distribution $f_\theta(x, p)$ given by, $\exp(\mp\alpha_\theta x)\delta(p \mp \text{Re}\sqrt{2\mu_\theta} \epsilon_\theta)$, where $\alpha_\theta$ is a positive-definite value dependent on $\theta$ and $\text{Im}\sqrt{2\mu_\theta}$. The mirror image distribution $\hat{f}_\theta(x, -p)$ locates the exponential tails in the opposite momentum half-axis, $\exp(\mp\alpha_\theta x)\delta(p \pm \text{Re}\sqrt{2\mu_\theta} \epsilon_\theta)$. Clearly, the product of the distributions $\exp(\mp\alpha_\theta x)\delta(p \pm \text{Re}\sqrt{2\mu_\theta} \epsilon_\theta)$ is given by an identical zero. The exclusion of the wavefunction tails, the shape of which is largely determined by the concrete value of $\theta$, from the definition of the complex energies is obviously sensible.

B. A quasi-classical error estimator for complex energies of resonances and bound states

Wigner representation indicates that the generalized inner product is determined by the overlap region of $f_\theta(x, p)$ and $\hat{f}_\theta(x, -p)$ in the phase-space. The overlap region may be defined by relatively small values of the distributions, as long as their displacements from the $x$-axis due to the complex scaling transformation turns out to be significant. When the values defining the overlap drop down to the computer round-off error, which corresponds to the fact that the corresponding computed wavefunction $f_\theta(x)$ is not able to reproduce the overlap phase-space region precisely, then the precision of the computed resonance complex energy $\epsilon_\theta$ is compromised. In the original formulation using wavefunctions [Eq. (24)] the decreased value of the generalized inner product of complex scaled wavefunctions is explained as due to a highly oscillatory behavior of the integrand, $f_\theta(x)^2$. Both phase-space and wavefunction formulations enable rigorous derivations of the presumable numerical errors of the energies $\epsilon_\theta$. Here,
we present an estimation, which is based on the phase-space formulation.

As the first step, we derive the numerical error $\delta_{\text{Wig}}^{\epsilon_\theta}$ for a hypothetical calculation of $\epsilon_\theta$ based on the phase-space formulation, Eq. (27). $\delta_{\text{Wig}}^{\epsilon_\theta}$ is not equal to the numerical error $\delta_{\epsilon_\theta}$, which would be obtained in a practical calculation given in the basis set representation, as defined by Eqs. (24) and (25). The relation between $\delta_{\text{Wig}}^{\epsilon_\theta}$ and $\delta_{\epsilon_\theta}$ will be discussed later. In the derivation of $\delta_{\text{Wig}}^{\epsilon_\theta}$, we resort to the so-called quasiclassical approximation, which has been described in works such as Refs. 91, 101–108. Within this approach, we expand the operator $\hat{\cal H}_\theta$ in the Taylor series such that,

$$\epsilon_\theta = H[e^{i_\theta x}, e^{-i_\theta p}] + \frac{1}{2} e^{i_\theta} V'(e^{i_\theta} x) \hat{\xi}^2 + \frac{1}{2} e^{-i_\theta} T'(e^{-i_\theta} p) \hat{\eta} + \ldots,$$

and neglect the expansion terms including higher powers of $\hbar$.

$$\epsilon_\theta = \frac{\int_{-\infty}^{\infty} dx dp H(e^{i_\theta x}, e^{-i_\theta p}) f_\theta(x, p)\bar{f}_\theta(x, p)}{\int_{-\infty}^{\infty} dx dp f_\theta(x, p)\bar{f}_\theta(x, p)}$$

(31)

Numerical precision of complex energies $\epsilon_\theta$ defined via Eq. (31) is limited by the numerical precision of the product of Wigner distributions given by

$$\delta_{\epsilon_\theta} = \delta_{f_\theta} \cdot [\bar{f}_\theta(x, p) + f_\theta(x, -p)],$$

(32)

where $\delta_{f_\theta}$ is a numerical precision of the Wigner distribution $\bar{f}_\theta(x, p)$. The corresponding numerical precision $\delta_{\text{Wig}}^{\epsilon_\theta}$ of the complex energy expectation value $\epsilon_\theta$ is given by

$$\delta_{\epsilon_\theta}^{\text{Wig}} = \delta_{f_\theta} \frac{\int_{-\infty}^{\infty} dx dp H(e^{i_\theta x}, e^{-i_\theta p}) (\bar{f}_\theta(x, p) + f_\theta(x, -p))}{\int_{-\infty}^{\infty} dx dp \bar{f}_\theta(x, p) f_\theta(x, p)}.$$

(33)

Equation (33) is simplified by its back-transforming into the wavefunction representation using the equalities, which can be derived based on rules described in Ref. 98,

$$\int_{-\infty}^{\infty} dx dp H(e^{i_\theta x}, e^{-i_\theta p}) f_\theta(x, p)$$

$$= \int_{-\infty}^{\infty} dx f_\theta(x) H \bar{f}_\theta(x) \equiv \langle \hat{\cal H}_\theta \rangle,$$

$$\int_{-\infty}^{\infty} dx dp H(e^{i_\theta x}, e^{-i_\theta p}) \bar{f}_\theta(x, p)$$

$$= \int_{-\infty}^{\infty} dx \bar{f}_\theta(x) H f_\theta(x) \equiv \langle \hat{\cal H}_\theta^* \rangle^*,$$

(34)

such that

$$\delta_{\epsilon_\theta}^{\text{Wig}} = \delta_{f_\theta} \frac{\int_{-\infty}^{\infty} dx f_\theta(x) \bar{f}_\theta(x) + \int_{-\infty}^{\infty} dx \bar{f}_\theta(x) H f_\theta(x)}{\left[\int dx f_\theta(x) \bar{f}_\theta(x)\right]^2}.$$

(35)

It is reasonable to assume that $\delta_{f_\theta}$ is proportional to the Euclidean norm,

$$\delta_{f_\theta} \propto \int_{-\infty}^{\infty} dx f_\theta^2(x) \bar{f}_\theta(x) \equiv \langle f_\theta | f_\theta \rangle.$$

(36)

The final result for the numerical error incurred in a hypothetical calculation using the Wigner phase-space definition of $\epsilon_\theta$ is given by,

$$\delta_{\epsilon_\theta}^{\text{Wig}} \propto \frac{\langle f_\theta | \bar{f}_\theta \rangle (\langle \hat{\cal H}_\theta \rangle + \langle \hat{\cal H}_\theta^* \rangle^*)}{(\langle f_\theta | f_\theta \rangle)^2}.$$

(37)

where $\langle f_\theta | f_\theta \rangle$ denotes the generalized norm of the resonance or bound state wavefunction $f_\theta(x)$. At this point a relation of $\delta_{\epsilon_\theta}^{\text{Wig}}$ and $\delta_{\epsilon_\theta}$, which would be obtained in a practical calculation, has to be defined. This relation is not given rigorously. We consider that the scalar product of the rotated Wigner distributions is given by a square of the corresponding generalized inner product of the wavefunctions. Therefore we assume that the numerical error of complex energies will be given approximately as a square-root of $\delta_{\epsilon_\theta}^{\text{Wig}}$ for computations based on a calculation of resonance wavefunctions, including the variational calculations,

$$\delta_{\epsilon_\theta} \approx \sqrt{\delta_{\epsilon_\theta}^{\text{Wig}}}.$$

(38)

IV. APPLICATION OF THE ERROR ESTIMATOR FOR A COMPUTATION OF CO2+ VIBRONIC RESONANCES

The use and validity of the obtained error estimator is demonstrated for an example of a complex scaling calculation of CO2+ vibronic resonances. This molecular diation predissociates rapidly due to the spin-orbit coupling with the life-time span from $10^{-5}$ to $10^{-3}$ seconds, depending on the vibrational excitation.51, 109 In the present calculation, the electronic basis set consists of the four lowest ($X^3\Sigma^+, a^1\Sigma^+, b^1\Pi$ a $3\Sigma^-$) states. Thanks to the previous work, we are able to readily use the analytical fits for the respective electronic potential curves and the spin orbit coupling elements calculated at the icMRCI/cc-pV6Z/AE level (see the supplementary material E-JCPSA6-124-008618 in Ref. 61). The basis set for the vibrational wavefunctions consists of the eigenfunctions of the finite box, where the matrix elements are obtained using the finite basis set representation.64

First, we illustrate the error calculations for a single resonance, which is defined by the $X^3\Pi$ electronic state and $v = 2$ vibrational number. The numerical error is evaluated in two different ways:

(i) directly by including a random error $\Omega$ to all elements of the complex Hamiltonian matrix,

$$H_{i,j} \rightarrow H_{i,j} \cdot (1 + \Omega),$$

(39)

prior to its diagonalization. The calculation with the perturbed Hamiltonian is repeated $N$ times, where $N = 500$, and the numerical error $\delta_{\epsilon_\theta}$ is evaluated as the standard deviation from the obtained mean complex energy eigenvalue.
using the error estimator as given in Eqs. (37) and (38). It allows us to relate the numerical error \( \delta_\epsilon \) for a nonzero \( \theta \), to a known error, \( \delta_\epsilon_0 \), for the case where \( \theta = 0 \):

\[
\delta_\epsilon = \delta_\epsilon_0 \sqrt{\frac{\langle f_0 | f_0 \rangle (\langle \hat{H}_0 \rangle + \langle \hat{H}_0^* \rangle) (f_0 | f_0 \rangle)}{2\langle f_0 | f_0 \rangle \langle \hat{H}_0 \rangle}}, \tag{40}
\]

\( \delta_\epsilon_0 \) is evaluated directly, using Eq. (39). Equation (40) is further simplified for the present case such that,

\[
\delta_\epsilon = \delta_\epsilon_0 \sqrt{\frac{\langle f_0 | f_0 \rangle (\langle \hat{H}_0 \rangle + \langle \hat{H}_0^* \rangle)}{2\langle \hat{H}_0 \rangle}}, \tag{41}
\]

where we take into account that the wavefunctions are normalized in the usual way (\( \langle f_0 | f_0 \rangle = 1 \) and \( f_0 | f_0 \rangle = 1 \)).

Results of the two methods (i) and (ii) are compared, where the method (i) serves as a benchmark calculation.

We perform three different calculations:

(i) Using a very small box size, which is given by the definition region, \( 1.7 \ a_0 \leq R \leq 4 \ a_0 \). This case requires the use of relatively large values of the complex scaling parameter, here \( \theta > 0.05 \), which are able to dampen the resonance wavefunction allowing it to fit into the small box. The larger value of \( \theta \) causes larger numerical errors, as predicted by Eq. (41), therefore this choice makes the problem of numerical error well exposed.

(ii) Using a large box size given by the definition region, \( 1.7 \ a_0 \leq R \leq 6 \ a_0 \). Here, the minimum value of the complex scaling parameter \( \theta \) leading to a converged complex energy is smaller than in the case (i), implying that this calculation is loaded with much smaller numerical error.

(iii) Using the small box size as used in the case (i), but the origin of complex scaling is shifted from the origin of coordinate axis to the bottom of the potential well \( R_0 = 2.3 \ a_0 \), such that \( R \rightarrow (R - R_0)e^{i\theta} + R_0 \). This measure helps to minimize distortions in the vibrational part of the resonance wavefunction, as is clear from the last example in Sec. II. Consequently, no significant increase of the numerical error with increasing \( \theta \) should occur in this case.

First, we inspect the dependence of \( \delta_\epsilon_0 \) on \( \Omega \) Eq. (39) for different number of basis functions and box sizes. We observe that \( \delta_\epsilon_0 \) is a linear function of \( |\Omega| \) given by

\[
\delta_\epsilon_0 = a \cdot |\Omega|, \tag{42}
\]

where the parameter \( a \) depends on the box size. It is given by \( a = 0.0095 \) and \( 0.01 \) for the small and large box sizes, respectively, see Fig. 5. Equation (42) holds until \( \delta_\epsilon_0 \) reaches the computer precision limit, for about \( |\Omega| = 10^{-12} \). Therefore the value of \( \delta_\epsilon_0 \) for \( |\Omega| = 5 \times 10^{-18} \) must be obtained by an extrapolation. Our calculations of \( \delta_\epsilon_0 \) further show that the numerical error is independent of the number of basis functions (see the comparison of calculations using 100 and 200 basis functions in Fig. 5). For this reason, the calculations reported below are converged with the number of basis functions each one separately, without affecting the study of numerical errors.

Then, we calculate the \( \theta \)-trajectories for all three cases (i)–(iii) described above. Our results are summarized in Fig. 6, where panels (a)–(c) show the obtained real parts of the resonance energy, while panels (d)–(f) show the obtained resonance lifetimes. The solid green curves show results obtained using statistics applied via Eq. (39), where \( |\Omega| = 10^{-13} \) – the energies and lifetimes being given as the means and the error-bars as the standard deviations. The dashed black curves show results obtained by the usual complex scaling method (without perturbing the Hamiltonian). Their error-bars are calculated using Eq. (41), where \( \delta_\epsilon_0 \) is estimated using Eq. (42). We observe two phenomena. First, the resonance energies and lifetimes show a \( \theta \)-dependence for small values of \( \theta \), although a theoretical critical value of \( \theta \) for this resonance is about zero, \( \theta_c \approx 9 \times 10^{-10} \) as obtained using the formula given by

\[
\theta_c = -\frac{1}{2} \arctan \frac{\text{Im} \epsilon_r}{\text{Re} \epsilon_r - \epsilon_0}, \tag{43}
\]

where \( \epsilon_r \) is the complex resonance energy and \( \epsilon_0 \) is the beginning of the corresponding rotated continuum. This can be explained by the fact that the resonance wavefunction must fit into a finite definition region, while the theoretical value applies for an infinite box. This is consistent with the observation that non-constant behavior is the shortest for the case of a large box (ii) and far the longest in the case (iii), where the damping effect of complex scaling is weak due to shifting of the complex scaling origin. Allow us to call the error that is due to insufficient size of the box compared to wavefunction, the stabilization error, \( \gamma_\theta \). We estimate it as the difference
between the calculated energy $\epsilon_\theta$ and energy $\epsilon_c$ that we would get for the same vibronic resonance if we were able to make a calculation based on the same set of electronic states with an infinite numerical precision. Dependence of the stabilization error $\gamma_\theta$ on the parameter $\theta$ is well illustrated on a logarithmic plot [Fig. (7)]. First, we observe an exponential decrease, which ends shortly after the stabilization error falls below the numerical error which will be described in detail in the next paragraph. The agreement of the both methods for calculating the resonance energy is even more evident on the logarithmic scale [Fig. (7)]. In the cases (i), (ii), and (iii) the complex resonance $X^3\Pi, \nu = 2$ as obtained in the most precise calculation ($d_0 = 2 \times 10^{-11}$), in the case (iii), where the effect of complex scaling on vibrational wavefunction is minimized, $\alpha = 3$ ($d_0 = 2 \times 10^{-10}$).

It is clear that the numerical calculation achieves a maximum accuracy when it minimizes both the stabilization and numerical errors simultaneously. This occurs at the intersection of these two errors, which are marked with the circles in Fig. 7. In the cases (i), (ii), and (iii) the complex resonance energy $\epsilon_\theta$ is obtained with different precisions $\delta_\theta$ given by $8.2 \times 10^{-9} \text{ cm}^{-1}$, $6 \times 10^{-10} \text{ cm}^{-1}$, and $3.6 \times 10^{-10} \text{ cm}^{-1}$, respectively. A comparison of accuracy that was achieved at a magnification of the box or shifting the complex scaling origin towards the approximate center of vibrational motion, demonstrates the great efficiency of the latter strategy. The change of the transformation origin leads to a reduction of the growth of the numerical error with the parameter $\theta$ for about forty times. Although this change is also accompanied by a slowdown of the decrease of the stabilization error $\gamma_\theta$ with $\theta$, this slowdown is only about twice.

The resonance position and lifetime for the resonance $X^3\Pi, \nu = 2$ as obtained in the most precise calculation (iii) are given by $\text{Re} \epsilon_\theta = 3549.283984322(5) \text{ cm}^{-1}$ and $\tau = 0.7165(0) \mu\text{s}$. The same strategy to maximize the numerical accuracy has also been applied for other vibronic resonances of the CO$^+$ molecular ion. The revised positions and lifetimes of these resonances are summarized in Table I and it should be noted that the corrections are relatively large compared to our previous study.\(^{51,109}\)
TABLE I. This table summarizes the energies and lifetimes of low-lying rovibrionic resonances of the CO$^{+2}$ ion, that are associated with the lowest electronic states. The presented results are obtained using the same electronic basis set that was used in our previous study (Ref. 61), however constitute an improvement of the vibrational calculation. The number of decimal places specified indicates the maximum accuracy obtained by applying the optimized complex scaling method (see the text).

<table>
<thead>
<tr>
<th>$v$</th>
<th>Position (cm$^{-1}$)</th>
<th>Life-time ($\mu$s)</th>
</tr>
</thead>
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<tr>
<td>$X^3\Pi$</td>
<td></td>
<td></td>
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<tr>
<td>0</td>
<td>732.294224457</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>1</td>
<td>2101.234257618</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>3549.283984322</td>
<td>0.7165</td>
</tr>
<tr>
<td>3</td>
<td>4884.341831278</td>
<td>1.091127$\times 10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>6168.657436793</td>
<td>2.8531659$\times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>7401.431588830</td>
<td>9.75680493$\times 10^{-6}$</td>
</tr>
<tr>
<td>$a^1\Sigma^+$</td>
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<td></td>
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<tr>
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<td>2169.319494358</td>
<td>$&gt; 10^4$</td>
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<tr>
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</tr>
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</tr>
<tr>
<td>3</td>
<td>7796.37638999</td>
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V. SUMMARY AND CONCLUSIONS

The complex scaling transformation has been studied using the Wigner phase-space representation. First, we have derived the phase-space operator, which converts the Wigner distribution of an original wavefunction to the distribution of the corresponding complex scaled wavefunction. We have found that the main effect of this operator is represented by an exponential modulation of the initial distribution, apparently causing the distribution to “rotate” in the phase-space along the origin of the transformation by the angle of $-\theta$, where $\theta$ is the complex scaling parameter. This finding reveals for the first time in detail how the complex scaling transformation operates on vibrational wavefunctions. So far, it was known only that this transformation causes unnatural oscillatory behavior of vibrational (or electronic) wavefunctions, while the reason for this effect has not been investigated or revealed. The emergence of the oscillatory behavior after the application of the transformation can now be clearly explained as a consequence of the exponential modulation (or apparent “rotation”) of the corresponding phase-space distribution, leading to the enhancement of higher momenta.

In the next part of our study we asked the natural question of how the distortion of vibrational parts of wavefunctions affects the computational accuracy of the variational complex scaling method. We rewrote the original formula for the complex variational energy into the Wigner representation. In doing this, the generalized inner product has been replaced by the scalar product of Wigner distributions, where the “right vector” is given by the Wigner distribution of the transformed resonance wavefunction, while the “left vector” is given by a mirror image of the same Wigner distribution, where the $x$-axis represents the axis of reflection. When we combine this with the fact that the transformation “rotates” the original Wigner distribution by the angle of $-\theta$, so the mirror Wigner distribution is “rotated” by the angle of $+\theta$, it is clear that the area of overlap of the two vectors is rapidly shrinking with increasing $\theta$. The accuracy of energy calculation is dependent on a good numerical representation of just this small area of overlap, which may be significantly impaired due to computer rounding error.

These considerations allowed us to propose a formula to estimate the computational error for the complex scaling method and thus verify our above-mentioned ideas on the actual calculation for which we chose the predissociation resonances of the CO$^{+2}$ dication. The correctness of the assumptions we made about the dominant role of the transformation in the development of computational errors have been fully confirmed. Above all, it turned out that the computational error grows approximately exponentially with the parameter $\theta$, while its growth is significantly affected by a relocation of the complex scaling origin. The increase of the numerical error can be very efficiently suppressed by shifting the transformation origin towards the center of vibrational motion. This observation, based on a rigorous derivation, explains the well-known fact that in the calculations of resonances by complex scaling much more stable results are obtained for $R \rightarrow (R - R_0)e^{i\theta} + R_0$, where $R_0$ is the bottom of the potential well, rather than for $R \rightarrow Re^{i\theta}$.

At the end, our study provides an intuitive know-how on how to set the parameters of numerical calculations of resonances using the complex scaling method to obtain results with maximum accuracy at a minimal computational cost.

ACKNOWLEDGMENTS

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APPENDIX: ANALYTICAL SOLUTION OF THE INTEGRAL IN EQ. (14)

In this Appendix we present algebraic manipulations, which lead from Eqs. (14) to (16). After substitution of Eq. (14) into Eq. (15) we get

$$\bar{w}_\theta(x’, p’; x, p) = (2\pi\hbar)^{-1} e^{-2px’ \sin \theta / \hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\sin \theta}{2\hbar} \right)^n$$

$$\times \int_{-\infty}^{\infty} d\Delta_x' e^{i\Delta_x'(p’ - p \cos \theta) / \hbar} \Delta_x'^n$$

$$\times \int_{-\hbar}^{\hbar} d\Delta_p e^{i\Delta_p(x’ \cos \theta - x) / \hbar} \Delta_p^m. \quad (A1)$$
After the integration, we obtain
\[
\tilde{w}_\theta(x', p'; x, p) = 2\pi \hbar e^{-2px'\sin\theta/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{\hbar \sin\theta}{2} \right)^n \\
\times \delta^{(n)}(p' - p \cos\theta) \delta^{(n)}(x' \cos\theta - x),
\]
(A2)
where \(\delta^{(n)}\) denotes the \(n\)th derivative of the Dirac \(\delta\)-function. Let us note that the kernel \(\tilde{w}_\theta(x', p'; x, p)\) includes an exponential function of the product \(px'\), where recall that \(x'\) is the kernel integration variable, while \(p\) is a mere parameter. We make the assumption that this exponential function can be replaced (using appropriate algebraic adjustments) by an exponential function of the product of the parameters, \(x p\). To replace the \(x'\) with \(x\), we utilize the derivatives of the \(\delta\)-function, \(\delta^{(n)}(x' \cos\theta - x)\), which are included in the sum. First, we customize them in this way,
\[
\delta^{(n)}(x' \cos\theta - x) = \frac{\delta^{(n)}(x' - x \cos^{-1}\theta)}{[\cos\theta]^n \cos^n\theta},
\]
(A3)
and obtain
\[
\tilde{w}_\theta(x', p'; x, p) = 2\pi \hbar e^{-2px'\sin\theta/\hbar} \sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{\hbar \tan\theta}{2} \right)^n \\
\times \delta^{(n)}(p' - p \cos\theta) \delta^{(n)}(x' - x \cos^{-1}\theta),
\]
(A4)
Then we use the identity given by
\[
e^{-2px'\sin\theta/\hbar} \delta^{(n)}(x' - x \cos^{-1}\theta) = e^{-2px \tan\theta/\hbar} \sum_{m=0}^{n} \binom{n}{m} \left( \frac{2p \sin\theta}{\hbar} \right)^{n-m} \\
\times \delta^{(m)}(x' - x \cos^{-1}\theta),
\]
(A5)
and obtain
\[
\tilde{w}_\theta(x', p'; x, p) = 2\pi \hbar e^{-2px \tan\theta/\hbar} \sum_{m=0}^{\infty} \frac{1}{m!} \frac{\hbar}{2} \\
\times \delta^{(m)}(p' - p \cos\theta) \delta^{(m)}(x' - x \cos^{-1}\theta) \\
\times \frac{1}{m!(n-m)!}.
\]
(A6)
The obtained equation can be simplified by reversing the order of the two sums, such that
\[
\tilde{w}_\theta(x', p'; x, p) = 2\pi \hbar e^{-2px \tan\theta/\hbar} \sum_{m=0}^{\infty} \frac{1}{m!} \\
\times \delta^{(m)}(x' - x \cos^{-1}\theta) \\
\times \sum_{n=m}^{\infty} \frac{(\sin^2\theta)^{n-m}}{\cos^2\theta} \delta^{(n)}(p' - p \cos\theta) \\
\times \frac{(n-m)!}{(n-m)!},
\]
(A7)