

Motion of wave-packets using the smooth-exterior-scaling complex potential

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Abstract

The motion of a Gaussian wave-packet is studied when absorbing complex potentials are added to the Hamiltonian in order to avoid the non-physical reflections which are obtained due to the use of a finite grid in numerical calculations. It is shown that the complex local potentials which were recently derived by the smooth-exterior-scaling (SES) method avoid reflections from the artificial potential walls. It is found that the SES complex potential is much more stable with respect to change in the kinetic energy of the wave-packet than other commonly used monomial local absorbing potentials. This is relevant to the study of dynamics in atomic, molecular or nuclear systems when there are several dominant open decay channels. © 1998 Elsevier Science B.V. All rights reserved.

Let us consider for demonstration purposes a Gaussian wave-packet that moves freely in 1D space. The time dependent solution of the Schrödinger equation is given by [1]:

$$\Psi_{\text{EXACT}}(x,t) = \left(\frac{2a^2}{\pi}\right)^{1/4} \frac{e^{i\phi}}{\left(a^4 + \frac{4\hbar^2 t^2}{m^2}\right)^{1/4}} e^{ik_0 x} \times \exp\left\{-\frac{\left[x - \frac{\hbar k_0}{m}t\right]^2}{a^2 + \frac{2i\hbar t}{m}}\right\}, \quad (1)$$

where

$$\phi = -\frac{1}{2}\arctan\left(\frac{2\hbar t}{ma^2}\right) - \frac{\hbar k_0^2}{2m}t. \quad (2)$$

Let us locate the initial Gaussian wave-packet inside

a box, which is given by $-L/2 \leq x \leq L/2$. As time passes, the wave-packet with initially positive momentum, $\hbar k_0$, gets out of the box, i.e. $|\Psi_{\text{EXACT}}(x,t)|^2 < 10^{-16}$ for $-L/2 \leq x \leq L/2$ and $t \geq T$. However, this is not the case when numerical calculations are carried out. In the numerical calculations x is varied from $-L/2$ to $L/2$. Therefore, reflections from the edges of the grid are obtained. To avoid these artificial reflections Leforestier and Wyatt proposed adding a negative imaginary potential to the Hamiltonian [2]. The imaginary potential they used was the Wood-Saxon potential which was well known in the nuclear physics literature. Neuhauser has shown that short range negative-imaginary potentials do as well as the Wood-Saxon and other types of absorbing potentials [3]. For the use of complex absorbing potentials rather than imaginary ones see, for example, Kosloff and Kosloff [4] and Ge and Zhang [5]. Riss and Meyer [6] have

derived closed formulas that describe the reflection and transmission effects accurately when an energy-dependent complex-absorbing-potential (CAP) is added to the Hamiltonian. From the requirement that the CAP in the reflection-free modified Hamiltonian will be linearly-energy-dependent, Riss and Meyer obtained a new effective Hamiltonian which consists of smooth-exterior-scaled kinetic operator and a potential term which vanishes (unlike the usual used CAPs) when the potential of interaction V vanishes as well. Their, so called, TCAP-method [7] is in fact similar to the smooth exterior complex scaling (SES) [8] except that they add an extra local complex potential which is problem dependent. In the absence of potential interaction, i.e. for free-particle Hamiltonians, the SES-CAP and T-CAP of Riss and Meyer are identical [7,9].

Here we use a new energy-independent and universal (i.e. not problem dependent) CAP that was derived by the use of the smooth-exterior-scaling method [10,11], which is based on the Moiseyev-Hirschfelder generalization of the complex coordinate method [12].

The smooth-exterior-scaling CAP is given by [8],

$$\hat{V}_{\text{SES}} = \frac{1}{2}V_1(x) \frac{\partial}{\partial x} + V_2(x) \frac{\partial^2}{\partial x^2}, \quad (3)$$

where

$$V_1(x) = \frac{\hbar^2}{mf^3(x)} \frac{\partial f(x)}{\partial x} \quad (4)$$

and

$$V_2(x) = \frac{\hbar^2}{2m}(1 - f^{-2}(x)). \quad (5)$$

$f(x)$ is the first-order derivative of the smooth-exterior-scaling path $F(x)$ and it is defined as [10–12]:

$$f(x) = \frac{\partial F(x)}{\partial x} = 1 + (e^{i\theta} - 1)g(x), \quad (6)$$

where $g(x)$ varies from 0 to 1 around the point $x = x_0$. We use here the complex-scaling-exterior path [10,11], such that

$$g(x) = 1 + \frac{1}{2}(\tanh[\lambda(x - x_0)] - \tanh[\lambda(x + x_0)]). \quad (7)$$

The smooth-exterior-scaling complex path $F(x)$ is obtained by carrying out integration over $g(x)$:

$$F(x) = x + (e^{i\theta} - 1) \times \left[x + \frac{1}{2\lambda} \ln \left(\frac{\cosh[\lambda(x - x_0)]}{\cosh[\lambda(x + x_0)]} \right) \right]. \quad (8)$$

The SES-CAP terms can be calculated using the above expression for $g(x)$ and the following analytical expression for the first derivative of $f(x)$ [10,11]:

$$\frac{\partial f(x)}{\partial x} = \frac{\lambda}{2}(e^{i\theta} - 1) \left(\frac{1}{\cosh^2[\lambda(x - x_0)]} - \frac{1}{\cosh^2[\lambda(x + x_0)]} \right). \quad (9)$$

When the basis functions $\phi_n(x)$ are used in the numerical calculation to represent the Hamiltonian and the initial wave-packet, then

$$\int_{-L/2}^{L/2} \Psi_{\text{EXACT}}(t=0) \phi_n^*(x) f^{-1/2}(x) dx \quad (10)$$

is the n -th component of the initial vector. This is due to the fact that the volume element here is $f(x)dx$ and

$$\int_{-L/2}^{L/2} \phi_n^*(x) \phi_{n'}(x) dx = \delta_{n,n'}. \quad (11)$$

However, one usually locates $\Psi_{\text{EXACT}}(x, t=0)$ in the non-complex-scaled region (i.e. where $g(x) \approx 0$ and $F(x) \approx x$). Therefore, $f^{-1/2}(x) \approx 1$ and there is no need to take into consideration the fact that the volume element is not dx .

In the case when one wishes to keep the volume element to be dx , then the SES-CAP should be redefined as [10,11]:

$$\hat{V}_{\text{SES}} = V_0(x) + V_1(x) \frac{\partial}{\partial x} + V_2(x) \frac{\partial^2}{\partial x^2}, \quad (12)$$

where

$$V_0(x) = \frac{\hbar^2}{4m} f^{-3}(x) \frac{\partial^2 f(x)}{\partial x^2} - \frac{5\hbar^2}{8m} f^{-4}(x) \times \left(\frac{\partial f(x)}{\partial x} \right)^2, \quad (13)$$

and

$$\frac{\partial^2 f(x)}{\partial x^2} = \lambda^2 (e^{i\theta} - 1) \left(\frac{\tanh[\lambda(x+x_0)]}{\cosh^2[\lambda(x+x_0)]} - \frac{\tanh[\lambda(x-x_0)]}{\cosh^2[\lambda(x-x_0)]} \right). \quad (14)$$

It should be mentioned that the use of the SES–CAP defined in Eq. (3) leads to complex non-symmetric Hamiltonian matrix, whereas the Hamiltonian matrix which is obtained when the SES–CAP defined in Eq. (12) is used, is a symmetric one. The diagonalization of complex symmetrical matrices is by about one order of magnitude faster than the diagonalization of complex general matrices [13]. Therefore we recommend the use of the SES–CAP defined in Eq. (12).

$V_1(x)$ and $V_2(x)$ are plotted in Fig. 1 for $\lambda = 0.2$, $\theta = 0.6$ and $x_0 = 390$. As one can see from Fig. 1, $V_1(x)$ is an extremely short range potential for the chosen value of λ . Since $V_1(x)$ looks like a delta function and since the flux operator is defined as $i\delta(x-x_0)\frac{\partial}{\partial x}$ we refer to the corresponding first term in the CAP which is defined in Eq. (3) as a flux-type operator. The second term is a kinetic-type operator, which describes the diffusion at $x \sim x_0$. As one can see from Fig. 1, $V_2(x)$ vanishes when $-x_0 < x < x_0$. The value of x_0 can be chosen such that only within this interval of x does the physical potential have

non-zero values and it vanishes elsewhere. The use of the universal flux-diffusion type CAP, which is constructed from the $V_1(x)$ and $V_2(x)$ functions which are presented in Fig. 1, enables us to obtain perfect reflection-free potentials as the box-size L is taken to infinity. However, the attractive part in the use of the complex-absorbing potentials is in the possibility of using small grids (i.e. small values of L) and still getting the correct dynamics which is obtained when $L = \infty$. It is clear that for finite values of L even the SES–CAP is not perfect.

To illustrate the usefulness of the universal flux-diffusion type CAP which is defined in Eq. (3) we compare it with the commonly used monomial local CAP (see, for example, Ref. [6]), which is defined as

$$\hat{V}_{\text{CAP}} = \begin{cases} -i\alpha(|x| - x_0)^3 & \text{when } |x| > x_0 \\ 0 & \text{elsewhere.} \end{cases} \quad (15)$$

We optimized the potential parameters in the CAPs (i.e. α in the monomial CAP and θ and x_0 in the SES–CAPs) to minimize the reflections from the edge of the grid (i.e. $x = \pm L/2$) at $t = T$, such that

$$\text{Error} = \int_{A_{\text{unscaled}}} dx |\Psi_{\text{NUM}}(x, T) - \Psi_{\text{EXACT}}(x, T)|^2 \quad (16)$$

is minimized. A_{unscaled} stands for the unscaled region in space. $t = T$ is the time it takes for the initial wave-packet to be reflected back and to be centered at the initial position, when no CAP is introduced in the numerical calculations. Note that for the monomial CAP there is only one parameter, x_0 , which determines where the CAP is turned on. In the case where the SES–CAP is used there are two parameters, λ and x_0 , which determine the point where the CAP is turned on. Therefore, the values of x_0 in the two CAPs can be different provided both CAPs are turned on at the same grid point. θ and x_0 (Eq. (9)) were optimized under the restriction that the SES–CAP turns on at the same value of x which was used for the monomial CAP.

First, let us illustrate the effect of the use of the SES–CAP on the propagation of a wave-packet. In Fig. 2 we show the shape of the propagated Gaussian as time passes. The dashed line stands for the exact dynamics obtained from Eq. (1), whereas the solid

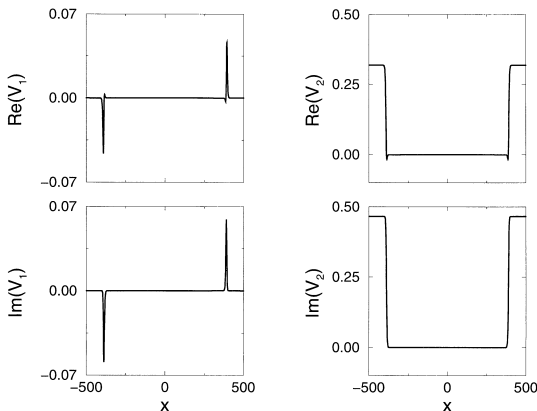


Fig. 1. $V_1(x)$ as function of x when the flux-type complex absorbing potential is defined as $V_1(x)(\partial/\partial x)$; and $V_2(x)$ as function of x when the diffusion-type complex absorbing potential is defined as $V_2(x)(\partial^2/\partial x^2)$.

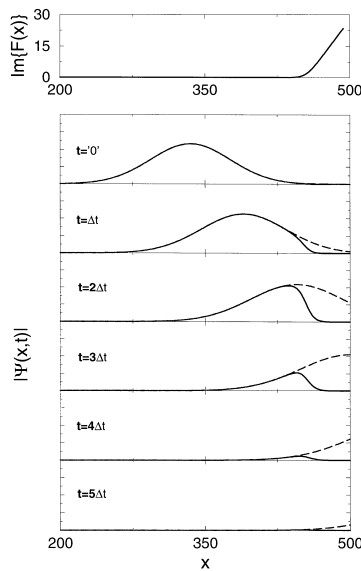


Fig. 2. Upper part of the plot: the imaginary part of the SES path $F(x)$, which provides the complex absorbing potential shown in Fig. 1, for $\theta = 0.55$, $\lambda = 0.11$, $x_0 = 455$ (see Eq. (8)). Lower part of the plot: the exact motion of the wave-packet (dashed line) and the numerical results (solid line) for $\hbar = 1$, $m = 1$, $a = 30\sqrt{2}$, $\langle E \rangle = (\hbar k_0)^2 / 2m = 0.1$ (see Eq. (1)) (atomic units are used throughout).

line stands for the results obtained from our numerical calculations where finite grid is used (i.e. particle-in-a-box basis functions with $L = 1000$ as the box size). At $t = 0$ the wave-packet is located at $x = 0$ and $t = '0'$ in Fig. 2 stands for a later time that is taken as a zero reference-time at which the wave-packet obtained from the numerical calculations is in an excellent agreement with the shape of the exact wave-packet. As one can see from the results presented in Fig. 2, the agreement between the numerical and the analytical results is excellent at any given time along the grid points where $\text{Im} F(x) \sim 0$. The SES-CAP is introduced only at the end of the grid (in the scale of our plot between $x = 455$ and the edge of the grid at $L/2 = 500$). In the region where the CAP is active the numerical wave-packet is absorbed and reflections from the edge of the grid are avoided.

The question we address ourselves is – how good are these CAPs when we use them for other initial conditions? Namely, how important it is to repeat the optimization procedure as we vary the parameters in

the studied problems? We held fixed the width of the initial wave-packets ($a = 30\sqrt{2}$) and k_0 (i.e. the mean kinetic energy of the wave-packet $\langle E \rangle$) in Eq. (1) was varied. The parameters in the CAPs were optimized for the value of k_0 for which $\langle E \rangle = 0.01$.

As one can see from the results presented in Fig. 3 for $\langle E \rangle = \langle E \rangle_{\text{opt}}$ all CAPs (monomial CAP and SES-CAPs) are good at preventing artificial reflections. However, when $\langle E \rangle = 0.1 \langle E \rangle_{\text{opt}}$ the error in the numerical calculations due to reflections is by 3 orders of magnitude smaller when the SES-CAP is used. When $\langle E \rangle = 10 \langle E \rangle_{\text{opt}}$ the use of the SES-CAP reduces the error by 5 orders of magnitude. The non expected result is that in both cases, where either monomial CAP or SES-CAP are used, the minimal error has not been obtained at $\langle E \rangle = \langle E \rangle_{\text{opt}}$. It implies that the results are sensitive to the CAP parameters for specific values of k_0 (i.e. $\langle E \rangle$), more than for the other values and there is a value of k_0 for which the CAP avoids reflection in a most efficient manner. Replacing the CAP given in Eq. (3) by the CAP given in Eq. (12) (for the case when the volume element is dx) results in similar errors. The main difference in the use of the different SES-CAPs is that at $\langle E \rangle = \langle E \rangle_{\text{opt}}$ the SES-CAP given in in Eq. (12) is the most efficient one. The important result, however, is the fact that the SES-CAP is far more efficient in avoiding artificial reflections when

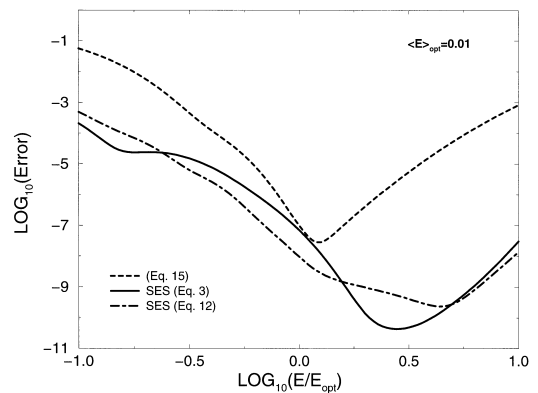


Fig. 3. The error (Eq. (16)) in the calculation of the wave-packet propagation using finite grid for two different CAPs. The CAPs parameters were optimized for an initial Gaussian wave-packet for which $\langle E \rangle = 0.01$, such that $\lambda = 0.2$, $\theta = 0.6$, $x_0 = 390$ for SES-CAP defined in Eq. (3), $\lambda = 0.28$, $\theta = 0.32$, $x_0 = 360$ for SES-CAP defined in Eq. (12) and $\alpha = 10^{-9}$, $x_0 = 300$ for monomial CAP (Eq. (15)).

the CAP parameters are held fixed, while several different wave-packets are propagated. This result is relevant to the case where there are several dominant open channels in the decaying process (either ionization or dissociation). In such a case, the wave-packet is a linear combination of out-going waves which move with different velocities (i.e. different values of k_0). Therefore, if CAPs which are similar to the monomial CAP we used, are inserted to the Hamiltonian to avoid reflections one should use different parameters for the CAPs which are associated with the different open channels for decay. That is, in the first step of the calculation the multi-dimensional potential is represented by a matrix, where the reaction coordinate x is the one free variable. In the next step of the calculation a diagonal matrix of complex monomial type CAPs is added. The CAPs on the diagonal are different in their parameters (i.e. different values of α). However, even in the case where there are several dominant open channels for decay a single and universal SES-CAP can be used. In the cases where one wishes to introduce the CAP in the interaction region where the potential of interaction is not equal to zero one should use the SES-CAP and replace the potential of interaction $V(x)$ by $V(F(x))$.

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References

- [1] C. Cohen-Tannoudji, B. Diu, F. Laboë, *Quantum Mechanics* Vol. 1, J. Wiley & Sons, 1977, p. 64.
- [2] C. Leforestier, R.E. Wyatt, *J. Chem. Phys.* 78 (1983) 2334.
- [3] D. Neuhauser, *J. Chem. Phys.* 103 (1995) 8513.
- [4] R. Kosloff, D. Kosloff, *J. Comp. Phys.* 63 (1986) 363.
- [5] J.-Y. Ge, J.Z.H. Zhang, *J. Chem. Phys.* 108 (1998) 1429.
- [6] U.V. Riss, H.-D. Meyer, *J. Chem. Phys.* 105 (1996) 1409.
- [7] U.V. Riss, H.-D. Meyer, *J. Phys. B* 28 (1995) 1475.
- [8] N. Rom, E. Engdahl, N. Moiseyev, *J. Chem. Phys.* 93 (1990) 3413.
- [9] U.V. Riss, H.-D. Meyer, *J. Phys. B* (submitted).
- [10] N. Moiseyev, *Phys. Rep. C* (1998) in press.
- [11] N. Moiseyev, *J. Phys. B* 31 (1998) 1431.
- [12] N. Moiseyev, J.O. Hirschfelder, *J. Chem. Phys.* 88 (1988) 1063.
- [13] I. Bar-On, V. Ryaboy, *SIAM J. Sci. Comput.* 18 (1997) 1412.