Siegert pseudostate formulation of scattering theory: General three-dimensional case

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This paper generalizes the Siegert pseudostate (SPS) formulation of scattering theory to arbitrary finite-range potentials without any symmetry in the three-dimensional (3D) case. The orthogonality and completeness properties of 3D SPSs are established. The SPS expansions for scattering states, outgoing-wave Green's function, scattering matrix, and scattering amplitude, that is, all major objects of scattering theory, are derived. The theory is illustrated by calculations for several model potentials. The results enable one to apply 3D SPSs as a purely discrete basis capable of representing both discrete and continuous spectra in solving various stationary and time-dependent quantum-mechanical problems.

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I. INTRODUCTION

Stationary scattering theory is usually formulated in terms of the bound and scattering states of a system under consideration represented by the discrete and continuous real-energy eigenstates of its Hamiltonian, respectively [1,2]. All physical observables can be expressed in terms of these states. Moreover, the set of these states possesses well-known orthogonality and completeness properties and can be used as a basis for expanding the solutions to more general problems, where the system interacts with some external forces. This approach, however, is not the only one possible. In 1939, in search of a formal derivation of the Breit-Wigner dispersion formula [3] from the Schrödinger equation, Siegert introduced [4] states that now bear his name. Siegert states (SSs) are also the eigenstates of the Hamiltonian, but satisfying a different boundary condition in the asymptotic region—the *outgoing-wave* boundary condition introduced in quantum mechanics by Gamow [5]. The Schrödinger equation supplemented by the requirement of regularity of the wave function and the outgoing-wave boundary condition constitute an eigenvalue problem (EVP) that has a purely discrete set of the generally complex-energy solutions. This EVP was first formulated for the generic problem of s-wave scattering by a central potential in Ref. [4], and its solutions are called the SSs. The set of SSs also possesses certain orthogonality and completeness properties. In particular, the bound states belong to the set and the scattering states can be expressed in terms of the SSs. This opens the way for an alternative formulation of scattering theory in terms of a purely discrete set of SSs.

There exists a vast literature on the theory of SSs and their applications in various physical problems. We mention only several pioneering studies [6–32] where the main results of the theory were obtained. This includes establishing the orthogonality and normalization condition for SSs [13,14,16–19,22–25,28,30], their completeness properties [18,19,25,27,30,31], expansions for the scattering states [10,28,30] and Green's function [20,22,25,27,29,30] in terms of SSs, expansions for the scattering matrix in the sum [7,15,29,30,32] and product [6,8] forms, the development of perturbation theory [7,14,16,21,22,25], and some generalizations to two-channel [11] and multichannel [12] problems. Summaries of the results can be found in Refs. [2,33–35]. In the majority of these studies the analysis is based on the argument of analyticity introduced in Ref. [7]: under certain conditions satisfied by the potential, the main objects of scattering theory, that is, scattering states, Green's function, and scattering matrix, are meromorphic functions of the particle's momentum having poles at the SS momentum eigenvalues, and then their expansions in terms of SSs follow from the Mittag-Leffler theorem [36]. The mathematically rigorous derivation and justification of the expansions is feasible only on the basis of ordinary differential equations; partial differential equations are hardly tractable in this sense. Therefore the majority of the results (with two important exceptions in Refs. [23,25] whose conditions of validity, however, are not established) are restricted to partial-wave scattering by central potentials and deduced from the analytic properties of the radial functions. These properties are very sensitive to the asymptotic behavior of the potential [9]. The conditions required for the SS expansions to hold are satisfied only for potentials decaying faster than any exponential function [8], which physically amounts to finite-range potentials. This is the main limitation of the theory of SSs.

A different approach to the theory of SSs was initiated in Ref. [37] where Siegert pseudostates (SPSs) were introduced. The SPSs are defined as a finite-basis representation of SSs for finite-range potentials. In a finite-basis representation the differential equations of the theory of SSs and scattering theory turn into algebraic equations. This approach has two important advantages. First, the algebraic equations are much simpler for the analysis than the differential equations, so the derivation of the results is greatly facilitated. The analysis yields relations expressing basic properties of SPSs and SPS expansions for the main objects of scattering theory that hold *exactly* for arbitrary dimension of the basis. In other words, they hold within the SPS formulation, which justifies the title of this and the previous papers of the series [38–40]. As the dimension of the basis grows and it becomes complete, these relations turn into the corresponding relations in terms of SSs. Second, the algebraic equations can be straightforwardly implemented in numerical calculations, which makes the theory applicable to practical problems. The theory of SPSs was thoroughly developed first for s-wave scattering by a central potential [38] and then generalized to s-wave scattering in the two-channel case [39] and partial-wave scattering with arbitrary angular

momentum [40]. In the first two cases perturbation theory was developed [41]. These studies reproduced all the known results of the theory of SSs and established a number of relations having no analogs in the previous literature, which proves the first of the above-mentioned advantages. The efficiency of the SPS approach in applications was demonstrated by calculations for a number of stationary [37–52] and time-dependent [53–62] problems. In particular, the approach was shown to compare favorably with other precision methods for calculating resonances in three-body Coulomb systems [37,42,44,46], to enable different computational techniques in studies of molecular dynamics [43,45,48–52] and laser-atom interaction [57,58,60–62], and to provide a framework for the asymptotic solution of the long-standing problem of nonadiabatic transitions to continuum [59].

In the present work the theory of SPSs [38–40] is generalized to arbitrary finite-range potentials without any symmetry in the three-dimensional (3D) case. The generalization is based on a partial-wave expansion of the 3D functions involved. In contrast to the spherically symmetric case treated in Refs. [38,40], now the different partial-wave components are coupled. It is remarkable that this coupling does not prevent the development of the theory.

The paper is organized as follows. In Sec. II, we define SPSs and establish their basic properties. In Sec. III, we derive the SPS expansions for the main objects of scattering theory. In Sec. IV, we illustrate the theory by calculations for several model potentials. Section V concludes the paper.

II. SIEGERT PSEUDOSTATES AND THEIR PROPERTIES

In this section, we specify the definition of SPSs for general potentials in the 3D case and establish their basic properties.

A. Siegert states

The stationary Schrödinger equation for a particle interacting with a potential $V(\mathbf{r})$ can be written in the form (a system of units in which Planck's constant and a particle's mass are equal to unity is used throughout)

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2}+\frac{\mathbf{l}^2}{2r^2}+V(\mathbf{r})-E\right]\phi(\mathbf{r})=0, \tag{1}$$

where $\mathbf{l}$ is the angular momentum operator and $\phi(\mathbf{r})$ is the particle's wave function multiplied by r. As in Refs. [38,40], we assume that the potential has a finite range,

$$V(\mathbf{r})|_{r>a}=0, \tag{2}$$

or decays sufficiently rapidly as r grows, so that cutting off its tail beyond $r=a$ does not produce any appreciable effect on the observables. However, in contrast to the spherically symmetric case treated in Refs. [38,40], here we consider arbitrary potentials without any symmetry. Following Siegert [4], the SSs are defined as the regular solutions to Eq. (1) satisfying the outgoing-wave boundary condition

$$\phi(\mathbf{r})|_{r\to\infty}\propto e^{ikr}, \tag{3}$$

where k is the momentum related to the energy E in Eq. (1) by

$$E=\tfrac{1}{2}k^2. \tag{4}$$

We consider generally complex values of k, including the case $\mathrm{Im}\,k<0$ when the exponent in Eq. (3) diverges at $r\to\infty$. A rigorist may argue that in this case the asymptotic condition (3) does not exclude an admixture of decaying solutions $\propto e^{-ikr}$. This difficulty can be eliminated for potentials satisfying Eq. (2). To this end, we expand $\phi(\mathbf{r})$ in a complete set of the eigenfunctions of $\mathbf{l}^2$. The standard spherical harmonics $Y_{lm}(\theta,\varphi)$ are not suitable for this purpose. They are complex and orthogonal with respect to Hermitian inner product involving complex conjugation, while complex conjugation is never used in the theory of SSs, since this operation is not analytic. Let us introduce the functions

$$X_{lm}(\theta,\varphi)=Y_{l0}(\theta,\varphi),\quad m=0, \tag{5a}$$

$$=\frac{1}{\sqrt{2}}[Y_{l|m|}(\theta,\varphi)+Y^*_{l|m|}(\theta,\varphi)],\quad m>0, \tag{5b}$$

$$=\frac{1}{i\sqrt{2}}[Y_{l|m|}(\theta,\varphi)-Y^*_{l|m|}(\theta,\varphi)],\quad m<0. \tag{5c}$$

We assume that $Y_{l0}(\theta,\varphi)$ is real, which is the case for commonly used phase conventions [63,64]. Then functions $X_{lm}(\theta,\varphi)$ provide a real orthonormal angular basis satisfying

$$I_\infty(\hat{\mathbf{r}},\hat{\mathbf{r}}')=\delta(\hat{\mathbf{r}}-\hat{\mathbf{r}}'), \tag{6}$$

where

$$I_L(\hat{\mathbf{r}},\hat{\mathbf{r}}')=\sum_\nu^L X_\nu(\hat{\mathbf{r}})X_\nu(\hat{\mathbf{r}}'). \tag{7}$$

Here and in the following, we use the shorthand notation

$$\hat{\mathbf{r}}=\mathbf{r}/r=(\theta,\varphi),\quad d\hat{\mathbf{r}}=\sin\theta d\theta d\varphi, \tag{8a}$$

$$\nu=(l,m),\quad \sum_\nu^L=\sum_{l=0}^L\sum_{m=-l}^l, \tag{8b}$$

and, similarly, $\hat{\mathbf{r}}'=\mathbf{r}'/r'$, $\nu'=(l',m')$, etc. The solutions to Eq. (1) can be expanded as

$$\phi(\mathbf{r})=\sum_\nu^\infty \phi_\nu(r)X_\nu(\hat{\mathbf{r}}). \tag{9}$$

Substituting this into Eq. (1), one obtains a set of coupled equations for the radial functions,

$$(T_l-E)\phi_\nu(r)+\sum_{\nu'}^\infty V_{\nu\nu'}(r)\phi_{\nu'}(r)=0, \tag{10}$$

where

$$T_l=-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}, \tag{11a}$$

$$V_{\nu\nu'}(r)=\int X_\nu(\hat{\mathbf{r}})V(\mathbf{r})X_{\nu'}(\hat{\mathbf{r}})\,d\hat{\mathbf{r}}. \tag{11b}$$

The regularity boundary condition for Eqs. (10) is

$$\phi_\nu(0)=0. \tag{12}$$

Taking into account Eq. (2), Eqs. (10) become decoupled in the outer region $r>a$. Then the outgoing-wave boundary

condition (3) can be specified as [40]

$$\phi_\nu(r)|_{r\geqslant a} = \phi_\nu(a)\frac{e_l(kr)}{e_l(ka)}, \tag{13}$$

or, equivalently,

$$\left(\frac{d}{dr} - ik + \frac{1}{r}\sum_{p=1}^{l}\frac{z_{lp}}{ikr + z_{lp}}\right)\phi_\nu(r)\bigg|_{r\geqslant a} = 0. \tag{14}$$

Here the function $e_l(z)$ is defined by

$$\left[\frac{d^2}{dz^2} - \frac{l(l+1)}{z^2} + 1\right]e_l(z) = 0, \tag{15a}$$

$$e_l(z)|_{z\to\infty} = e^{iz}, \tag{15b}$$

and given by [65]

$$e_l(z) = e^{iz}\frac{\theta_l(-iz)}{(-iz)^l}, \quad \theta_l(z) = \prod_{p=1}^{l}(z - z_{lp}), \tag{16}$$

where $\theta_l(z)$, $l = 0,1,\ldots,$ are the reverse Bessel polynomials [67] and z_{lp}, $p = 1,\ldots,l$ are the zeros of $\theta_l(z)$. Equations (10), (12), and (14) can be satisfied simultaneously only for a discrete set of generally complex values of k, so we deal with an EVP. The SSs are the solutions to this EVP. The momentum eigenvalues and partial-wave radial eigenfunctions are denoted by k_n and $\phi_{\nu n}(r)$, where n enumerates the SSs. The corresponding energy eigenvalues E_n and full 3D eigenfunctions $\phi_n(\mathbf{r})$ are then given by Eqs. (4) and (9).

Due to the condition (2), Eqs. (10) in the outer region $r > a$ can be treated analytically, which enables one to exclude this region from consideration by incorporating the outgoing-wave boundary condition (14) into the equations. This can be done by means of the Bloch operator [68]. Let us introduce the function and derivative value operators at $r = a$,

$$\mathcal{F} = \delta(r-a), \quad \mathcal{D} = \delta(r-a)\frac{d}{dr}. \tag{17}$$

Then Eqs. (10) can be presented in the form

$$\left[\tilde{T}_l - \frac{1}{2}\left(ik - \frac{1}{a}\sum_{p=1}^{l}\frac{z_{lp}}{ika + z_{lp}}\right)\mathcal{F} - \frac{k^2}{2}\right]\phi_\nu(r) + \sum_{\nu'}^{\infty} V_{\nu\nu'}(r)\phi_{\nu'}(r) = 0, \tag{18}$$

where

$$\tilde{T}_l = T_l + \tfrac{1}{2}\mathcal{D}. \tag{19}$$

It is sufficient to consider Eqs. (18) in the inner region $r \leqslant a$, the solutions automatically satisfy Eq. (14). This form of the SS EVP is most convenient for the following.

B. Siegert pseudostates

Let $\mathcal{H}$ denote the Hilbert space of functions of $\mathbf{r}$ for which radial functions in the partial-wave expansion of the form (9) are square integrable in the interval $0 \leqslant r \leqslant a$ and satisfy Eq. (12). The SSs belong to $\mathcal{H}$. Let $f_i(r)$, $i = 1,2,\ldots$ be a set of real functions satisfying

$$f_i(0) = 0, \tag{20a}$$

$$\int_0^a f_i(r) f_{i'}(r)\,dr = \delta_{ii'}, \tag{20b}$$

$$I_\infty(r,r') = \delta(r-r'), \quad 0 \leqslant r, r' \leqslant a, \tag{20c}$$

where

$$I_N(r,r') = \sum_{i=1}^{N} f_i(r) f_i(r'). \tag{21}$$

The products of $f_i(r)$ and $X_\nu(\hat{\mathbf{r}})$ provide a real orthonormal basis in $\mathcal{H}$. To define SPSs, we employ finite basis sets,

$$f_i(r), \quad i = 1,2,\ldots,N, \tag{22a}$$

$$X_\nu(\hat{\mathbf{r}}), \quad \nu = (0,0),(1,-1),\ldots,(L,L), \tag{22b}$$

where all $\sum_\nu^L 1 = (L+1)^2$ angular functions with $l \leqslant L$ are included [see the notation (8b)]. The products of these functions span a subspace $\mathcal{H}_{NL} \in \mathcal{H}$ of dimension $N(L+1)^2$. The unity operator in this subspace is represented by $I_N(r,r')I_L(\hat{\mathbf{r}},\hat{\mathbf{r}}')$. The SPSs are a representation of the SSs in $\mathcal{H}_{NL}$. Retaining in the sum over ν' in Eqs. (18) only terms with $l' \leqslant L$ and seeking the solution in the form

$$\phi_\nu(r) = \sum_{i=1}^{N} c_{i\nu} f_i(r), \quad 0 \leqslant r \leqslant a, \tag{23}$$

we arrive at the algebraic EVP,

$$\left[\tilde{\mathbf{T}}_l - \frac{1}{2}\left(\lambda - \frac{1}{a}\sum_{p=1}^{l}\frac{z_{lp}}{\lambda a + z_{lp}}\right)\mathbf{F} + \frac{\lambda^2}{2}\mathbf{I}\right]\mathbf{c}_\nu + \sum_{\nu'}^{L}\mathbf{V}_{\nu\nu'}\mathbf{c}_{\nu'} = \mathbf{0}. \tag{24}$$

Here

$$\lambda = ik, \tag{25}$$

$\mathbf{c}_\nu$ is a column vector of length N composed of the coefficients $c_{i\nu}$ in Eq. (23), $\tilde{\mathbf{T}}_l$, $\mathbf{V}_{\nu\nu'}$, and $\mathbf{F}$ are real symmetric matrices of dimension $N \times N$ representing the operators $\tilde{T}_l$, $V_{\nu\nu'}(r)$, and $\mathcal{F}$, respectively, and having the elements

$$\tilde{T}_{ii',l} = \int_0^a f_i(r)\tilde{T}_l f_{i'}(r)\,dr = \frac{1}{2}\int_0^a \frac{df_i(r)}{dr}\frac{df_{i'}(r)}{dr}\,dr + \int_0^a f_i(r)\frac{l(l+1)}{2r^2}f_{i'}(r)\,dr, \tag{26a}$$

$$V_{ii',\nu\nu'} = \int_0^a f_i(r)V_{\nu\nu'}(r)f_{i'}(r)\,dr, \tag{26b}$$

$$F_{ii'} = \int_0^a f_i(r)\mathcal{F}f_{i'}(r)\,dr = f_i(a)f_{i'}(a), \tag{26c}$$

and $\mathbf{I}$ is an $N \times N$ unit matrix representing the operator (21). Throughout the paper, $\mathbf{0}$ denotes a generally rectangular zero matrix of appropriate dimension, e.g., a zero vector of length N in Eq. (24). Let $\mathbf{f}$ be a vector with the elements

$$f_i = f_i(a), \quad i = 1,2,\ldots,N. \tag{27}$$

Then, using Eq. (23), the partial-wave surface amplitude is given by

$$\phi_\nu(a) = \mathbf{f}^T \mathbf{c}_\nu = \mathbf{c}_\nu^T \mathbf{f}, \tag{28}$$

and Eq. (26c) can be written as

$$\mathbf{F} = \mathbf{f}\mathbf{f}^T, \tag{29}$$

where T stands for transpose. Equation (24) is a representation of the SS EVP (18) in the finite basis (22). The SPSs are the solutions to Eq. (24). The SPS eigenvalues and eigenvectors in the finite-basis representation are denoted by λ_n and $\mathbf{c}_{\nu n}$. The SPSs belong to $\mathcal{H}_{NL}$. Since the basis (22) becomes complete in $\mathcal{H}$ as N and L grow, the SPSs converge to the SSs in the limit $N \to \infty$ and $L \to \infty$. However, we emphasize that for any finite N and L the SPSs and SSs are distinct. The SPSs depend on N and L and hence present a more general set. All the relations below in this section are derived in the finite-basis representation for SPSs, expressed in terms of λ_n and $\mathbf{c}_{\nu n}$, and hold for any N and L. The final formulas are given also in the coordinate representation. In this case, we use the same notation k_n and $\phi_{\nu n}(r)$ for SPSs as for SSs; this does not lead to ambiguities since it is always clear which set is meant. The transformation between the two representations is defined by Eqs. (23) and (25); in the outer region, the functions $\phi_{\nu n}(r)$ are given by Eq. (13). Setting in the final formulas $N \to \infty$ and $L \to \infty$, one obtains corresponding relations in the basis-independent form in terms of SSs.

We mention that the matrices $\mathbf{V}_{\nu\nu'}$ with $\nu \neq \nu'$ couple the different partial waves in Eq. (24). For spherically symmetric potentials these matrices vanish, the different ν become decoupled, and then the set of the 3D SPSs splits into independent subsets of partial-wave SPSs studied in Ref. [40].

C. Distribution of the eigenvalues

Some general properties of the distribution of the SPS eigenvalues λ_n in complex λ plane can be deduced from Eq. (24) without solving the equation. First, using the properties of matrices $\tilde{\mathbf{T}}_l$, $\mathbf{V}_{\nu\nu'}$, and $\mathbf{F}$ and the fact that the set of the zeros z_{lp} for a given l coincides with the complex conjugate set [67], it can be seen that if λ is an eigenvalue of Eq. (24) then λ^* also is an eigenvalue. This means that the eigenvalues λ_n are either pure real or occur in complex conjugate pairs λ_n and λ_n^*. Second, multiplying Eq. (24) from the left by $\mathbf{c}_\nu^{*T}$, summing up over ν, and taking the imaginary part of the result, we obtain

$$\mathrm{Im}(\lambda) \sum_\nu^L \left[2\,\mathrm{Re}(\lambda) \mathbf{c}_\nu^{*T} \mathbf{c}_\nu - \omega_l(-\lambda a) |\mathbf{f}^T \mathbf{c}_\nu|^2 \right] = 0, \tag{30}$$

where $\omega_0(z) = 1$ and

$$\omega_l(z) = 1 + \sum_{p=1}^{l} \frac{z_{lp}}{(z - z_{lp})(z^* - z_{lp})}, \quad l \geqslant 1. \tag{31}$$

For any l, this function is real for all complex z and takes positive values in the half plane $\mathrm{Re}\, z > 0$ [40]. Then it follows from Eq. (30) that the eigenvalues λ_n are either pure real or lie in the half plane $\mathrm{Re}\,\lambda > 0$. Summarizing and translating the conclusions to complex k plane, we obtain that the SPS momentum eigenvalues k_n are either pure imaginary or occur in pairs k_n and $-k_n^*$ lying in the lower half plane. As seen from Eq. (13), the position of k_n determines the character of the asymptotic behavior of $\phi_{\nu n}(r)$. Thus SPSs can be divided into four groups:

$$\begin{array}{lll} \text{bound:} & \mathrm{Re}\, k_n = 0, & \mathrm{Im}\, k_n > 0, \\ \text{antibound:} & \mathrm{Re}\, k_n = 0, & \mathrm{Im}\, k_n < 0, \\ \text{outgoing:} & \mathrm{Re}\, k_n > 0, & \mathrm{Im}\, k_n < 0, \\ \text{incoming:} & \mathrm{Re}\, k_n < 0, & \mathrm{Im}\, k_n < 0. \end{array} \tag{32}$$

Since the argumentation does not depend on N and L, the conclusions hold also for the SS eigenvalues k_n. We note that Eq. (24) may have nontrivial solutions with $\mathrm{Re}\,\lambda = \mathrm{Im}\, k = 0$ and $\mathrm{Im}\,\lambda \neq 0$, provided that $\mathbf{f}^T \mathbf{c}_\nu = \phi_\nu(a) = 0$ for all ν, which complies with Eq. (30). Such SPSs correspond to bound states embedded into the continuum.

D. Linearization

The SPS EVP (24) is nonlinear with respect to the eigenvalue λ. The nonlinearity not only prevents solving this equation by standard methods of linear algebra, but even makes it not obvious how many solutions exist. Here we linearize Eq. (24) by extending the dimension of the corresponding Hilbert space. The idea of this step was employed in the theory of SSs in Ref. [26]. The linearization procedure described below generalizes a similar construction used in Refs. [38,40] and is essential for the theory of SPSs.

Let $\mathcal{H}_N$ be a functional space spanned by the radial basis (22a). It is isomorphic to the N-dimensional space of partial-wave vectors $\mathbf{c}_\nu$. For simplicity, we do not distinguish the two spaces and write $\mathbf{c}_\nu \in \mathcal{H}_N$. The solutions to Eq. (24) are vectors of length $N(L+1)^2$ combining all $\mathbf{c}_\nu$ in the order listed in Eq. (22b),

$$\begin{pmatrix} \mathbf{c}_{00} \\ \dots \\ \mathbf{c}_{LL} \end{pmatrix} \in \mathcal{H}_{NL} = \prod_\nu^L \mathcal{H}_N. \tag{33}$$

The space $\mathcal{H}_{NL}$ is a direct product of $(L+1)^2$ copies of $\mathcal{H}_N$, one for each of the angular basis functions. However, for constructing the SPSs it is convenient to combine the partial-wave components in a different way. Let us introduce the quantities [40]

$$\xi_{\nu p} = -\frac{z_{lp} \mathbf{f}^T \mathbf{c}_\nu}{\lambda a + z_{lp}}, \quad p = 1, \dots, l, \tag{34}$$

and extended partial-wave vectors of length $2N + l$,

$$\mathbb{C}_\nu = \begin{pmatrix} \mathbf{c}_\nu \\ \lambda \mathbf{c}_\nu \\ \xi_{\nu 1} \\ \dots \\ \xi_{\nu l} \end{pmatrix} \in \mathcal{H}_N^{(l)} = \mathcal{H}_N^2 \times \mathcal{C}^l. \tag{35}$$

The extended partial-wave space $\mathcal{H}_N^{(l)}$ is a direct product of two copies of $\mathcal{H}_N$, one for each of the vectors $\mathbf{c}_\nu$ and $\lambda \mathbf{c}_\nu$, and l copies of the set of complex numbers $\mathcal{C}$ corresponding to $\xi_{\nu p}$. We also introduce square matrices of dimension

$(2N+l)\times(2N+l)$,

$$\mathbb{S}_{\nu\nu}=\begin{pmatrix}\mathbf{0} & \mathbf{I} & \mathbf{0} & \dots & \mathbf{0}\\ -2(\tilde{\mathbf{T}}_l+\mathbf{V}_{\nu\nu}) & \mathbf{F} & \mathbf{f}/a & \dots & \mathbf{f}/a\\ -z_{l1}\mathbf{f}^T/a & \mathbf{0} & -z_{l1}/a & \dots & 0\\ \dots & \dots & \dots & \dots & \dots\\ -z_{ll}\mathbf{f}^T/a & \mathbf{0} & 0 & \dots & -z_{ll}/a\end{pmatrix}, \tag{36a}$$

and rectangular matrices of dimension $(2N+l)\times(2N+l')$,

$$\mathbb{S}_{\nu\nu'}=\begin{pmatrix}\mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0}\\ -2\mathbf{V}_{\nu\nu'} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & 0 & \dots & 0\\ \dots & \dots & \dots & \dots & \dots\\ \mathbf{0} & \mathbf{0} & 0 & \dots & 0\end{pmatrix}, \quad \nu\neq\nu'. \tag{36b}$$

The structure of these matrices is determined by that of the vector (35), namely: the first two blocks in the first two rows are square matrices of dimension $N\times N$; the further blocks in the same rows are columns of length N; the first two blocks in the following rows are rows of length N; finally, the remaining block in Eq. (36a) is a diagonal matrix of dimension $l\times l$ and the corresponding block in Eq. (36b) is a zero matrix of dimension $l\times l'$. We next introduce a vector combining the different partial-wave vectors (35) ordered following the list (22b),

$$\mathbb{C}=\begin{pmatrix}\mathbb{C}_{00}\\ \dots\\ \mathbb{C}_{LL}\end{pmatrix}\in\mathcal{H}_{NL}^{\mathrm{SPS}}=\prod_{\nu}^{L}\mathcal{H}_N^{(l)}, \tag{37}$$

and a matrix consisting of the blocks (36a) and (36b) ordered in the same way,

$$\mathbb{S}=\begin{pmatrix}\mathbb{S}_{00,00} & \dots & \mathbb{S}_{00,LL}\\ \dots & \dots & \dots\\ \mathbb{S}_{LL,00} & \dots & \mathbb{S}_{LL,LL}\end{pmatrix}. \tag{38}$$

Using this notation, we can rewrite the SPS EVP (24) in the form

$$(\mathbb{S}-\lambda)\mathbb{C}=\mathbf{0}. \tag{39}$$

This is a linear EVP with respect to the eigenvalue λ. The price for the linearization is the extension of the Hilbert space from $\mathcal{H}_{NL}$ of dimension $N(L+1)^2$ to $\mathcal{H}_{NL}^{\mathrm{SPS}}$ of dimension

$$N_{\mathrm{SPS}}=\sum_{\nu}^{L}(2N+l)=2N(L+1)^2+\frac{1}{6}L(L+1)(4L+5). \tag{40}$$

This is the dimension of the EVP (39). Thus, there exists N_{SPS} solutions of Eq. (39) which we also call SPSs and denote by

$$\lambda_n,\ \mathbb{C}_n,\quad n=1,2,\dots,N_{\mathrm{SPS}}. \tag{41}$$

The eigenvalues λ_n coincide with the eigenvalues of Eq. (24); the eigenvectors $\mathbb{C}_n$ are determined by λ_n and the eigenvectors $\mathbf{c}_{\nu n}$ of Eq. (24) according to Eqs. (34), (35), and (37); the corresponding quantities (34) are denoted by $\xi_{\nu pn}$.

Equation (39) is suitable for calculating SPSs by means of standard linear algebra routines. However, for establishing the properties of SPSs it is convenient to transform this equation to a symmetric form. Let us introduce a partial-wave weight matrix having the same structure as $\mathbb{S}_{\nu\nu}$ in Eq. (36a),

$$\mathbb{W}_l=\begin{pmatrix}-\mathbf{F} & \mathbf{I} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{I} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & -1/z_{l1} & \dots & 0\\ \dots & \dots & \dots & \dots & \dots\\ \mathbf{0} & \mathbf{0} & 0 & \dots & -1/z_{ll}\end{pmatrix}. \tag{42}$$

Let $\mathbb{W}$ be a matrix having the same structure as $\mathbb{S}$ in Eq. (38) with the blocks defined by

$$\mathbb{W}_{\nu\nu}=\mathbb{W}_l, \tag{43a}$$

$$\mathbb{W}_{\nu\nu'}=\mathbf{0},\quad \nu\neq\nu'. \tag{43b}$$

The matrix $\mathbb{W}$ is complex (because the zeros z_{lp} are generally complex) and symmetric. We introduce one more matrix of the same structure,

$$\tilde{\mathbb{S}}=\mathbb{W}\mathbb{S}, \tag{44}$$

with the blocks

$$\tilde{\mathbb{S}}_{\nu\nu}=\mathbb{W}_l\mathbb{S}_{\nu\nu}=\begin{pmatrix}-2(\tilde{\mathbf{T}}_l+\mathbf{V}_{\nu\nu}) & \mathbf{0} & \mathbf{f}/a & \dots & \mathbf{f}/a\\ \mathbf{0} & \mathbf{I} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{f}^T/a & \mathbf{0} & 1/a & \dots & 0\\ \dots & \dots & \dots & \dots & \dots\\ \mathbf{f}^T/a & \mathbf{0} & 0 & \dots & 1/a\end{pmatrix}, \tag{45a}$$

$$\tilde{\mathbb{S}}_{\nu\nu'}=\mathbb{W}_l\mathbb{S}_{\nu\nu'}=\begin{pmatrix}-2\mathbf{V}_{\nu\nu'} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & 0 & \dots & 0\\ \dots & \dots & \dots & \dots & \dots\\ \mathbf{0} & \mathbf{0} & 0 & \dots & 0\end{pmatrix},\ \nu\neq\nu'. \tag{45b}$$

This matrix is real and symmetric. Multiplying Eq. (39) from the left by $\mathbb{W}$, we obtain

$$(\tilde{\mathbb{S}}-\lambda\,\mathbb{W})\mathbb{C}=\mathbf{0}. \tag{46}$$

This is a generalized EVP with symmetric matrices. The orthogonality and completeness properties of SPSs immediately follow from this equation.

E. Orthogonality and normalization condition

Assuming that all SPS eigenvalues λ_n are distinct, the solutions to Eq. (46) are orthogonal with respect to the inner product

$$\mathbb{C}_n^T\,\mathbb{W}\mathbb{C}_{n'}=2\lambda_n\delta_{nn'}, \tag{47}$$

where the coefficient on the right-hand side is chosen to obtain the usual normalization condition for bound states [see Eq. (51) below]. Substituting here Eqs. (35), (37), and (43), we obtain

$$\sum_{\nu}^{L}\left(\mathbf{c}_{\nu n}^T\mathbf{c}_{\nu n'}-\frac{1}{\lambda_n+\lambda_{n'}}\left[\mathbf{c}_{\nu n}^T\mathbf{F}\mathbf{c}_{\nu n'}+\sum_{p=1}^{l}\frac{\xi_{\nu pn}\xi_{\nu pn'}}{z_{lp}}\right]\right)=\delta_{nn'}. \tag{48}$$

Equation (47) shows that vectors $\mathbb{C}_n$ belonging to the extended space $\mathcal{H}_{NL}^{\mathrm{SPS}}$ are orthogonal with the weight $\mathbb{W}$, in the usual sense of the word in linear algebra, while projecting this equation to the original space $\mathcal{H}_{NL}$ results in an unusual

orthonormalization condition (48) for $\mathbf{c}_{\nu n}$. In the coordinate representation Eq. (48) reads

$$\sum_{\nu}^{L}\left(\int_0^a \phi_{\nu n}(r)\phi_{\nu n'}(r)\,dr + i\frac{\phi_{\nu n}(a)\phi_{\nu n'}(a)}{k_n+k_{n'}}\left[1+\sum_{p=1}^{l}\frac{z_{lp}}{(ik_na+z_{lp})(ik_{n'}a+z_{lp})}\right]\right)=\delta_{nn'}. \tag{49}$$

Using Eq. (14), this condition can be rewritten as

$$\int\left(\int_0^a \phi_n(\mathbf{r})\phi_{n'}(\mathbf{r})\,dr + \frac{\phi_{n'}(\mathbf{r})\partial\phi_n(\mathbf{r})/\partial r-\phi_n(\mathbf{r})\partial\phi_{n'}(\mathbf{r})/\partial r}{k_n^2-k_{n'}^2}\bigg|_{r=a}\right)d\hat{\mathbf{r}}=\delta_{nn'}. \tag{50}$$

Using Eq. (13), it can be shown that if both n and n' correspond to bound SPSs then Eq. (50) reduces to

$$\int \phi_n(\mathbf{r})\phi_{n'}(\mathbf{r})\,dr\,d\hat{\mathbf{r}}=\delta_{nn'}, \tag{51}$$

which coincides with the usual orthonormalization condition for bound states. Equations (50) and (51) do not contain N and L, and hence apply also to SSs.

The derivation of the normalization condition for SSs was a profound problem in the development of the theory, because all but bound SS eigenfunctions exponentially diverge at $r\to\infty$; see Eq. (3). The different authors [13,14,16,17,19,23] used different procedures to regularize the normalization integral. In the most general form the orthonormalization condition for SSs was obtained from Hilbert's identity in Ref. [23]. For finite-range potentials satisfying Eq. (2) this condition coincides with Eq. (50).

F. Completeness relations

The solutions to Eq. (46) form a complete set in $\mathcal{H}_{NL}^{\mathrm{SPS}}$. Taking into account Eq. (47), this fact is expressed by

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\mathbb{C}_n\mathbb{C}_n^T}{2\lambda_n}=\mathbb{W}^{-1}, \tag{52}$$

where $\mathbb{W}^{-1}$ is the inverse of $\mathbb{W}$. This matrix has the same block-diagonal structure as $\mathbb{W}$ in Eqs. (43) with the diagonal blocks given by

$$(\mathbb{W}^{-1})_{\nu\nu}=\mathbb{W}_l^{-1}=\begin{pmatrix}\mathbf{0}&\mathbf{I}&\mathbf{0}&\dots&\mathbf{0}\\ \mathbf{I}&\mathbf{F}&\mathbf{0}&\dots&\mathbf{0}\\ \mathbf{0}&\mathbf{0}&-z_{l1}&\dots&0\\ \dots&\dots&\dots&\dots&\dots\\ \mathbf{0}&\mathbf{0}&0&\dots&-z_{ll}\end{pmatrix}. \tag{53}$$

Thus Eq. (52) amounts to the relations

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\mathbf{c}_{\nu n}\mathbf{c}_{\nu' n}^T}{\lambda_n}=\mathbf{0}, \tag{54a}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\mathbf{c}_{\nu n}\mathbf{c}_{\nu' n}^T=2\mathbf{I}\delta_{\nu\nu'}, \tag{54b}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\lambda_n\mathbf{c}_{\nu n}\mathbf{c}_{\nu' n}^T=2\mathbf{F}\delta_{\nu\nu'}, \tag{54c}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\xi_{\nu pn}\mathbf{c}_{\nu' n}}{\lambda_n}=\mathbf{0}, \tag{54d}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\xi_{\nu pn}\mathbf{c}_{\nu' n}=\mathbf{0}, \tag{54e}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\xi_{\nu pn}\xi_{\nu' p' n}}{\lambda_n}=-2z_{lp}\delta_{pp'}\delta_{\nu\nu'}. \tag{54f}$$

We again see that vectors $\mathbb{C}_n$ form a complete set in the extended space $\mathcal{H}_{NL}^{\mathrm{SPS}}$, in the usual sense of the word, while their projections $\mathbf{c}_{\nu n}$ to the original space $\mathcal{H}_{NL}$ satisfy unusual completeness relations (54). In the coordinate representation, these relations read

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_n(\mathbf{r})\phi_n(\mathbf{r}')}{ik_n}=0, \tag{55a}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\phi_n(\mathbf{r})\phi_n(\mathbf{r}')=2I_N(r,r')I_L(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \tag{55b}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}ik_n\phi_n(\mathbf{r})\phi_n(\mathbf{r}')=2I_N(r,a)I_N(r',a)I_L(\hat{\mathbf{r}},\hat{\mathbf{r}}'), \tag{55c}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_{\nu n}(a)\phi_{\nu' n}(r)}{ik_n(ik_na+z_{lp})}=0, \tag{55d}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_{\nu n}(a)\phi_{\nu' n}(r)}{ik_na+z_{lp}}=0, \tag{55e}$$

$$\sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_{\nu n}(a)\phi_{\nu' n}(a)}{ik_n(ik_na+z_{lp})(ik_na+z_{l'p'})}=-\frac{2}{z_{lp}}\delta_{pp'}\delta_{\nu\nu'}, \tag{55f}$$

where $0\leqslant r,r'\leqslant a$. Equations (54) and (55) express the completeness properties of SPSs. The corresponding properties of SSs follow from Eqs. (55) in the limit $N\to\infty$ and $L\to\infty$, which amounts to extending the summations to infinity and substituting Eqs. (6) and (20c).

The completeness properties of SSs was another profound problem. Indeed, Eq. (55a) shows that the set of SSs is overcomplete in $\mathcal{H}$, which hindered the derivation of the SS expansions for various objects in scattering theory. The properties analogous to Eqs. (55a) and (55b) were first established for a δ-function potential and $l=0$ in Ref. [27] and then proved for a more general class of central potentials and arbitrary l in Ref. [31]. The properties analogous to Eqs. (55c)–(55f) were established for central potentials and arbitrary l within the SPS formulation in Ref. [40]. The

present analysis generalizes all these properties to arbitrary finite-range potentials.

G. Spectral matrix and its properties

Let $\mathbf{M}(\lambda)$ denote the matrix of dimension $N(L+1)^2 \times N(L+1)^2$ multiplying the vector (33) in Eq. (24). This matrix consists of partial-wave blocks $\mathbf{M}_{\nu\nu'}(\lambda)$ of dimension $N \times N$ given by

$$\mathbf{M}_{\nu\nu'}(\lambda) = \left[\tilde{\mathbf{T}}_l - \frac{1}{2}\left(\lambda - \frac{1}{a}\sum_{p=1}^{l}\frac{z_{lp}}{\lambda a + z_{lp}}\right)\mathbf{F} + \frac{\lambda^2}{2}\mathbf{I}\right]\delta_{\nu\nu'} + \mathbf{V}_{\nu\nu'}. \tag{56}$$

We call $\mathbf{M}(\lambda)$ the spectral matrix because its determinant turns to zero whenever λ coincides with one of the SPS eigenvalues λ_n. To calculate the determinant, we note that matrix (29) has rank 1, and hence it can be reduced by an orthogonal transformation of the radial basis (22a) to the diagonal form with only one nonzero element. The determinant of $\mathbf{M}(\lambda)$ is not affected by the transformation, of course. Multiplying the columns of $\mathbf{M}(\lambda)$ containing the nonzero element of $\mathbf{F}$ by $\theta_l(-\lambda a)$, we obtain a matrix whose elements are polynomials in λ. Calculating the coefficient of the highest power of λ in the determinant of this matrix, we find

$$\det[\mathbf{M}(\lambda)] = \prod_{\nu}^{L}\frac{(-a)^l}{2^N\theta_l(-\lambda a)} \times \prod_{n=1}^{N_{\rm SPS}}(\lambda - \lambda_n). \tag{57}$$

The inverse matrix $\mathbf{M}^{-1}(\lambda)$ can be expressed in the form of a spectral resolution in terms of the eigenvalues and eigenvectors of Eq. (24). Its partial-wave blocs are given by

$$(\mathbf{M}^{-1})_{\nu\nu'}(\lambda) = \sum_{n=1}^{N_{\rm SPS}}\frac{\mathbf{c}_{\nu n}\mathbf{c}^T_{\nu' n}}{\lambda_n(\lambda - \lambda_n)}. \tag{58}$$

The validity of this formula can be verified using Eqs. (24) and (54).

For the following, we need some additional properties of $\mathbf{M}(\lambda)$. From Eq. (56) using a property of the reverse Bessel polynomials [40] we obtain

$$\mathbf{M}_{\nu\nu'}(\lambda) - \mathbf{M}_{\nu\nu'}(-\lambda) = -\frac{\lambda(i\lambda a)^{2l}}{\theta_l(\lambda a)\theta_l(-\lambda a)}\mathbf{F}\delta_{\nu\nu'}. \tag{59}$$

This means the equality of two matrices of the same dimension as $\mathbf{M}(\lambda)$ whose partial-wave blocks stand on the left- and right-hand sides of Eq. (59). Let $\mathbf{\Theta}(\lambda)$ denote a diagonal matrix consisting of the partial-wave blocks $\mathbf{\Theta}_{\nu\nu'}(\lambda) = (i\lambda a)^{-l}\theta_l(\lambda a)\mathbf{I}\delta_{\nu\nu'}$, and $\tilde{\mathbf{M}}(\lambda) = \mathbf{\Theta}(-\lambda)\mathbf{M}(\lambda)$. Multiplying the equality from the left by $\mathbf{\Theta}(\lambda)$ and from the right by $\tilde{\mathbf{M}}^{-1}(\lambda) = \mathbf{M}^{-1}(\lambda)\mathbf{\Theta}^{-1}(-\lambda)$, we obtain

$$(-1)^l\left[\frac{\theta_l(\lambda a)}{\theta_l(-\lambda a)}\mathbf{I}\delta_{\nu\nu'} + \frac{\lambda(-i\lambda a)^{l+l'}}{\theta_l(-\lambda a)\theta_{l'}(-\lambda a)}\mathbf{F}(\mathbf{M}^{-1})_{\nu\nu'}(\lambda)\right] = [\tilde{\mathbf{M}}(-\lambda)\tilde{\mathbf{M}}^{-1}(\lambda)]_{\nu\nu'}. \tag{60}$$

Two important identities follow from this equation. Let us multiply Eq. (60) from the left by a row $\mathbf{f}^T$ and from the right by a vector $\mathbf{f}$ and divide by a number $\mathbf{f}^T\mathbf{f}$,

$$(-1)^l\tilde{S}_{\nu\nu'}(\lambda) = (\mathbf{f}^T\mathbf{f})^{-1}\mathbf{f}^T[\tilde{\mathbf{M}}(-\lambda)\tilde{\mathbf{M}}^{-1}(\lambda)]_{\nu\nu'}\mathbf{f}, \tag{61}$$

where

$$\tilde{S}_{\nu\nu'}(\lambda) = \frac{\theta_l(\lambda a)}{\theta_l(-\lambda a)}\delta_{\nu\nu'} + \frac{\lambda(-i\lambda a)^{l+l'}}{\theta_l(-\lambda a)\theta_{l'}(-\lambda a)}\mathbf{f}^T(\mathbf{M}^{-1})_{\nu\nu'}(\lambda)\mathbf{f}. \tag{62}$$

Equation (61) means the equality of two matrices of dimension $(L+1)^2 \times (L+1)^2$. The matrices depend on λ, and the equality remains valid under changing the sign of λ. We multiply the matrices from the right by themselves taken at $-\lambda$. It can be seen that $\mathbf{f}$ is an eigenvector of the partial-wave block standing on the left-hand side of Eq. (60), and hence the same holds for the right-hand side. From this we obtain

$$\sum_{\nu''}^{L}\mathbf{f}^T[\tilde{\mathbf{M}}(-\lambda)\tilde{\mathbf{M}}^{-1}(\lambda)]_{\nu\nu''}\mathbf{f}\mathbf{f}^T[\tilde{\mathbf{M}}(\lambda)\tilde{\mathbf{M}}^{-1}(-\lambda)]_{\nu''\nu'}\mathbf{f} = (\mathbf{f}^T\mathbf{f})^2\delta_{\nu\nu'} \tag{63}$$

and the first identity

$$\sum_{\nu''}^{L}(-1)^l\tilde{S}_{\nu\nu''}(\lambda)(-1)^{l''}\tilde{S}_{\nu''\nu'}(-\lambda) = \delta_{\nu\nu'}. \tag{64}$$

From Eq. (60) using (57) we find

$$\det\left[\frac{\theta_l(\lambda a)}{\theta_l(-\lambda a)}\mathbf{I}\delta_{\nu\nu'} + \frac{\lambda(-i\lambda a)^{l+l'}}{\theta_l(-\lambda a)\theta_{l'}(-\lambda a)}\mathbf{F}(\mathbf{M}^{-1})_{\nu\nu'}(\lambda)\right] = \prod_{n=1}^{N_{\rm SPS}}\frac{\lambda_n + \lambda}{\lambda_n - \lambda}. \tag{65}$$

The matrix in the square brackets has dimension $N(L+1)^2 \times N(L+1)^2$. Using Sylvester's determinant theorem [69], the left-hand side of this equation can be rewritten in terms of the determinant of a matrix of dimension $(L+1)^2 \times (L+1)^2$, which yields the second identity

$$\det[\tilde{S}_{\nu\nu'}(\lambda)] = \prod_{n=1}^{N_{\rm SPS}}\frac{\lambda_n + \lambda}{\lambda_n - \lambda}. \tag{66}$$

III. STATIONARY SCATTERING THEORY

In this section, we derive the SPS expansions for all major objects of stationary scattering theory, thus reformulating the theory in terms of SPSs.

A. Bound states and resonances

The bound states are the regular solutions of Eq. (1) decaying at $r \to \infty$. They are represented by the bound SPSs, see Eq. (32), and determined in terms of the corresponding eigenvectors $\mathbf{c}_{\nu n}$ and eigenvalues $\lambda_n = ik_n$ by the partial-wave expansion (9) truncated to a finite L, Eq. (23) in the inner region, and Eqs. (13) and (28) in the outer region.

Depending on the shape of the potential in Eq. (1), there may exist resonances. Such states are represented by the outgoing SPSs whose momentum and energy eigenvalues satisfy

$$|\operatorname{Im} k_n| \ll \operatorname{Re} k_n, \tag{67a}$$

$$E_n = \mathcal{E}_n - \frac{i}{2}\Gamma_n, \quad \Gamma_n \ll \mathcal{E}_n, \tag{67b}$$

where $\mathcal{E}_n$ and Γ_n are the energy and width of the resonance, respectively. A resonance is an asymptotic notion, that is, it

can be rigorously defined only in the presence of some small parameter that justifies the above inequalities, as is the case, e.g., for shape resonances in the semiclassical approximation. When the parameter tends to zero, $\mathrm{Im}\, k_n$ and Γ_n also tend to zero and the resonance turns into a bound state embedded into the continuum. As was mentioned in Sec. II C, for such a state $\mathbf{f}^T\mathbf{c}_{\nu n} = \phi_{\nu n}(a) = 0$ for all ν, and then from Eq. (48) we obtain $\sum_\nu^L \mathbf{c}_{\nu n}^T\mathbf{c}_{\nu n} = 1$. If the parameter is small but not exactly zero, then $\phi_{\nu n}(a)$ is not exactly zero either. By expanding Eq. (30) in this case we obtain

$$\Gamma_n = \sum_\nu^L \Gamma_{\nu n}, \tag{68}$$

where

$$\Gamma_{\nu n} = \mathrm{Re}(k_n)\,\omega_l(-ik_n a)|\phi_{\nu n}(a)|^2 \tag{69}$$

is the partial width for decay into channel ν. We emphasize that these equations hold only asymptotically in the limit $\Gamma_n \to 0$, when the resonance becomes well defined.

As the dimensions N and L of the basis grow, the SPSs representing bound states and resonances converge to the corresponding SSs. They converge also with respect to the cutoff radius a in Eq. (2), provided that the potential decays sufficiently rapidly as $r \to \infty$. Only these SPSs are physically meaningful individually. All the other SPSs essentially depend on a and serve to form a complete set for expanding the continuum. These convergence properties are discussed in more detail in Sec. IV.

B. Outgoing-wave Green's function

The outgoing-wave Green's function multiplied by r and r' satisfies

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{\mathbf{l}^2}{2r^2} + V(\mathbf{r}) - E\right]G(\mathbf{r},\mathbf{r}';k) = \delta(r-r')\delta(\hat{\mathbf{r}}-\hat{\mathbf{r}}'). \tag{70}$$

Similarly to Eqs. (9) and (10), we seek the solution in the form

$$G(\mathbf{r},\mathbf{r}';k) = \sum_{\nu\nu'}^{\infty} G_{\nu\nu'}(r,r';k)X_\nu(\hat{\mathbf{r}})X_{\nu'}(\hat{\mathbf{r}}'), \tag{71}$$

and obtain a set of coupled equations for the radial functions,

$$(T_l - E)G_{\nu\nu'}(r,r';k) + \sum_{\nu''}^{\infty} V_{\nu\nu''}(r)G_{\nu''\nu'}(r,r';k) = \delta(r-r')\delta_{\nu\nu'}. \tag{72}$$

The regularity and outgoing-wave boundary conditions can be formulated similarly to Eqs. (12) and (14), respectively,

$$G_{\nu\nu'}(0,r';k) = 0, \tag{73a}$$

$$\left(\frac{d}{dr} - ik + \frac{1}{r}\sum_{p=1}^{l}\frac{z_{lp}}{ikr + z_{lp}}\right)G_{\nu\nu'}(r,r';k)\bigg|_{r\geqslant a,\, r'<r} = 0. \tag{73b}$$

Retaining in the sum over ν'' in Eq. (72) only terms with $l'' \leqslant L$ and substituting

$$G_{\nu\nu'}(r,r';k) = \sum_{i,i'=1}^{N} G_{i\nu,i'\nu'}(\lambda)f_i(r)f_{i'}(r'), \quad 0 \leqslant r,r' \leqslant a, \tag{74}$$

we obtain an algebraic representation of Eqs. (70) and (73) in the finite basis (22),

$$\left[\tilde{\mathbf{T}}_l - \frac{1}{2}\left(\lambda - \frac{1}{a}\sum_{p=1}^{l}\frac{z_{lp}}{\lambda a + z_{lp}}\right)\mathbf{F} + \frac{\lambda^2}{2}\mathbf{I}\right]\mathbf{G}_{\nu\nu'}(\lambda) + \sum_{\nu''}^{L}\mathbf{V}_{\nu\nu''}\mathbf{G}_{\nu''\nu'}(\lambda) = \mathbf{I}\delta_{\nu\nu'}, \tag{75}$$

where $\mathbf{G}_{\nu\nu'}(\lambda)$ is a matrix of dimension $N \times N$ composed of the coefficients $G_{i\nu,i'\nu'}(\lambda)$ in Eq. (74). Taking into account Eqs. (56) and (58), the solution to Eq. (75) is given by

$$\mathbf{G}_{\nu\nu'}(\lambda) = \sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\mathbf{c}_{\nu n}\mathbf{c}_{\nu' n}^T}{\lambda_n(\lambda - \lambda_n)}. \tag{76}$$

In the coordinate representation we obtain

$$G_{\nu\nu'}(r,r';k) = \sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_{\nu n}(r)\phi_{\nu' n}(r')}{k_n(k_n - k)}, \quad 0 \leqslant r,r' \leqslant a. \tag{77}$$

In the outer region from Eq. (73b) we have

$$G_{\nu\nu'}(r,r';k)|_{r\geqslant a,\, r'<r} = G_{\nu\nu'}(a,r';k)\frac{e_l(kr)}{e_l(ka)}. \tag{78}$$

These equations together with the symmetry property $G_{\nu\nu'}(r,r';k) = G_{\nu'\nu}(r',r;k)$ define the radial functions for all r and r'. In the 3D form Eq. (77) reads

$$G(\mathbf{r},\mathbf{r}';k) = \sum_{n=1}^{N_{\mathrm{SPS}}}\frac{\phi_n(\mathbf{r})\phi_n(\mathbf{r}')}{k_n(k_n - k)}, \quad 0 \leqslant r,r' \leqslant a. \tag{79}$$

This is the SPS expansion for the outgoing-wave Green's function. As $N \to \infty$ and $L \to \infty$, it turns into the corresponding expansion in terms of SSs. The SS analog of Eq. (79) was first given in Ref. [25] and later justified rigorously for central potentials in Refs. [27,29,30].

C. Partial-wave scattering states and scattering matrix

Let us introduce a matrix $\varphi_{\nu\nu'}(r,k)$ satisfying

$$(T_l - E)\varphi_{\nu\nu'}(r,k) + \sum_{\nu''}^{\infty}V_{\nu\nu''}(r)\varphi_{\nu''\nu'}(r,k) = 0, \tag{80a}$$

$$\varphi_{\nu\nu'}(0,k) = 0, \tag{80b}$$

$$\varphi_{\nu\nu'}(r,k)|_{r\geqslant a} = e^{i\pi l/2}e_l(-kr)\delta_{\nu\nu'} - e^{-i\pi l/2}e_l(kr)S_{\nu\nu'}(k). \tag{80c}$$

The columns of $\varphi_{\nu\nu'}(r,k)$ are the regular solutions of Eq. (10) having an incoming wave with the amplitude $e^{i\pi l'/2}$ only in channel ν' and outgoing waves with amplitudes

$-e^{-i\pi l/2}S_{\nu\nu'}(k)$ in all channels ν; see Eq. (15b). Thus ν enumerates the partial-wave components of a solution and ν' enumerates the different solutions. These solutions are called the partial-wave scattering states and $S_{\nu\nu'}(k)$ is the scattering matrix. We also introduce the matrix Jost solutions $F_{\pm,\nu\nu'}(r,k)$ of Eq. (80a) satisfying the boundary condition

$$F_{\pm,\nu\nu'}(r,k)|_{r\geqslant a} = e^{\mp i\pi l/2}e_l(\pm kr)\delta_{\nu\nu'}. \tag{81}$$

These solutions taken at an arbitrary k are not regular, i.e., do not satisfy Eq. (80b). To simplify the notation, let us temporarily drop the subscripts of the matrices introduced. The solution of Eqs. (80) can be expressed in terms of the Jost solutions,

$$\varphi(r,k) = F_-(r,k) - F_+(r,k)S(k), \quad 0 \leqslant r < \infty. \tag{82}$$

The Jost solutions satisfy the identities [2,39]

$$F_+(r,k)F_-^T(r,k) - F_-(r,k)F_+^T(r,k) = 0 \tag{83}$$

and

$$\frac{dF_+(r,k)}{dr}F_-^T(r,k) - \frac{dF_-(r,k)}{dr}F_+^T(r,k) = 2ik, \tag{84}$$

where, again, T stands for transpose. Using these equations, it can be shown [39] that the Green's matrix $G(r,r';k)$ composed of the radial functions in Eq. (71) is given by

$$G(r,r';k) = \frac{i}{k}[\theta(r'-r)\varphi(r,k)F_+^T(r',k) + \theta(r-r')F_+(r,k)\varphi^T(r',k)]. \tag{85}$$

Setting here $r' = a$ and taking into account that $F_+(a,k)$ is diagonal, we find

$$\varphi(r,k) = -ikG(r,a;k)F_+^{-1}(a,k), \quad 0 \leqslant r \leqslant a. \tag{86}$$

Substituting Eqs. (77) and (81) and restoring the subscripts, we obtain

$$\varphi_{\nu\nu'}(r,k) = -ike^{-ika}\frac{(ka)^{l'}}{\theta_{l'}(-ika)}\sum_{n=1}^{N_{\rm SPS}}\frac{\phi_{\nu n}(r)\phi_{\nu' n}(a)}{k_n(k_n-k)}, \quad 0 \leqslant r \leqslant a. \tag{87}$$

This is the SPS expansion for the partial-wave scattering states. From Eqs. (82) and (86), requiring continuity of $\varphi(r,k)$ at $r = a$, we find

$$S(k) = F_+^{-1}(a,k)[F_-(a,k) + ikG(a,a;k)F_+^{-1}(a,k)]. \tag{88}$$

Restoring the subscripts, we obtain

$$S_{\nu\nu'}(k) = e^{-2ika}\left[\frac{\theta_l(ika)}{\theta_l(-ika)}\delta_{\nu\nu'} + \frac{ik(ka)^{l+l'}}{\theta_l(-ika)\theta_{l'}(-ika)} \times \sum_{n=1}^{N_{\rm SPS}}\frac{\phi_{\nu n}(a)\phi_{\nu' n}(a)}{k_n(k_n-k)}\right]. \tag{89}$$

This is the SPS expansion for the scattering matrix. Following Refs. [38,40], we call it the *sum* formula. Note that this matrix is explicitly symmetric,

$$S_{\nu\nu'}(k) = S_{\nu'\nu}(k), \tag{90}$$

as it should be. It can be seen that the matrix in the square brackets in Eq. (89) is the coordinate representation of the matrix (62). Then, using Eq. (64), we obtain that for any complex k the scattering matrix satisfies

$$\sum_{\nu''}^{L}(-1)^l S_{\nu\nu''}(k)(-1)^{l''}S_{\nu''\nu'}(-k) = \delta_{\nu\nu'}. \tag{91}$$

For real k, we have from Eq. (89)

$$S_{\nu\nu'}(-k) = (-1)^{l+l'}S^*_{\nu\nu'}(k), \tag{92}$$

and Eq. (91) takes the form

$$\sum_{\nu''}^{L}S_{\nu\nu''}(k)S^*_{\nu''\nu'}(k) = \delta_{\nu\nu'}. \tag{93}$$

This together with Eq. (90) means unitarity of the scattering matrix. We emphasize that all the important properties of the scattering matrix expressed by Eqs. (90)–(93) hold exactly for any N and L, i.e., they hold within the SPS formulation. Translating Eq. (66) to the coordinate representation and comparing with Eq. (89) we obtain

$$\det[S_{\nu\nu'}(k)] = e^{-2ika(L+1)^2}\prod_{n=1}^{N_{\rm SPS}}\frac{k_n+k}{k_n-k}. \tag{94}$$

This is the SPS expansion for the determinant of the scattering matrix. Following Refs. [38,40], we call it the *product* formula. Let us introduce the eigenphase shift sum $\delta(k)$ defined by [2]

$$\det[S_{\nu\nu'}(k)] = \exp[2i\delta(k)], \tag{95}$$

and the scattering length $\alpha = -\delta(k)/k|_{k\to 0}$. From Eq. (94) we obtain

$$\alpha = (L+1)^2 a + \sum_{n=1}^{N_{\rm SPS}}\frac{i}{k_n}. \tag{96}$$

Although k_n are complex, the properties of their distribution discussed in Sec. II C ensure that α is real.

As $N \to \infty$ and $L \to \infty$, Eqs. (87), (89), (94), and (96) turn into the corresponding expansions in terms of SSs. The SS analog of Eq. (87) was obtained for s-wave scattering by a central potential in Ref. [10] and later rederived by a different method in Ref. [28]. It was generalized to arbitrary partial waves within the SPS formulation in Ref. [40]. Many authors [7,15,29,30,32] attempted to derive the SS analog of the sum formula (89). However, the resulting formulas always contained some undefined quantities such as an entire function, some residues, or matrix elements, which make them useless for practical applications. As far as we know, in the closed form free from uncertainties the SS analog of Eq. (89) was obtained within the SPS formulation first for s-wave [38] and then for arbitrary partial wave [40]. The SS analog of the product formula (94) was given without due proof for s-wave scattering in Ref. [6] and later derived rigorously for potentials decaying faster than any exponential function using Hadamard's form of the Weierstrass expansion theorem [36] in Ref. [8]. It was generalized to arbitrary partial waves within the SPS formulation in Ref. [40]. Importantly, all these studies considered central potentials. Equations (87), (89), (94), and (96) and their SS analogs emerging in the limit $N \to \infty$ and $L \to \infty$ apply to potentials without any symmetry and, as such, do not have counterparts in the literature.

TABLE I. Effective masses m_x and m_y defining the potential (103) (in all cases $m_z = 1$ and $\gamma = 0.1$), ground-state energies E, and scattering lengths α (in atomic units) for the four models considered in the present calculations. The sets (a,N,L) give the minimum values of the parameters for which the results converged.

			Ground-state energy		Scattering length	
Model	m_x	m_y	E	(a,N,L)	α	(a,N,L)
A	1	1	−0.407 058 030 6	(14,15,0)	21.562 842	(240,45,0)
B	0.5	0.5	−0.221 414 845 8	(17,35,10)	−16.558 611	(300,100,20)
C	2	2	−0.686 396 950 2	(11,35,10)	30.357 074	(320,110,20)
D	2	0.5	−0.385 615 488 9	(15,40,14)	18.459 755	(300,100,24)

D. Scattering amplitude and cross sections

To define scattering observables, we need to introduce scattering states with definite asymptotic momentum $\mathbf{k}$ [1,2]. Such states multiplied by r satisfy

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{\mathbf{l}^2}{2r^2} + V(\mathbf{r}) - E\right]\psi(\mathbf{r},\mathbf{k}) = 0, \tag{97a}$$

$$\psi(\mathbf{r},\mathbf{k})|_{r\to\infty} = re^{i\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k},\hat{\mathbf{r}})e^{ikr}, \tag{97b}$$

where $f(\mathbf{k},\hat{\mathbf{r}})$ is the scattering amplitude. It can be shown by standard methods [1,2] that

$$\psi(\mathbf{r},\mathbf{k}) = \frac{2i\pi}{k}\sum_{\nu,\nu'}^{\infty} e^{i\pi l'/2}\varphi_{\nu\nu'}(r,k)X_\nu(\hat{\mathbf{r}})X_{\nu'}(\hat{\mathbf{k}}) \tag{98}$$

and

$$f(\mathbf{k},\hat{\mathbf{r}}) = \sum_{\nu,\nu'}^{\infty} e^{i\pi(l'-l)/2} f_{\nu\nu'}(k)X_\nu(\hat{\mathbf{r}})X_{\nu'}(\hat{\mathbf{k}}), \tag{99}$$

where

$$f_{\nu\nu'}(k) = \frac{2i\pi}{k}[\delta_{\nu\nu'} - S_{\nu\nu'}(k)]. \tag{100}$$

The differential scattering cross section is given by

$$\frac{d\sigma(\mathbf{k})}{d\hat{\mathbf{r}}} = |f(\mathbf{k},\hat{\mathbf{r}})|^2, \tag{101}$$

and the total cross section is

$$\sigma(\mathbf{k}) = \int |f(\mathbf{k},\hat{\mathbf{r}})|^2 d\hat{\mathbf{r}} = \sum_{\nu\nu'\nu''}^{\infty} e^{i\pi(l'-l'')/2} f_{\nu\nu'}(k) f^*_{\nu\nu''}(k)X_{\nu'}(\hat{\mathbf{k}})X_{\nu''}(\hat{\mathbf{k}}). \tag{102}$$

Truncating these partial-wave expansions to finite L and substituting Eqs. (87) and (89), one obtains the corresponding expansions in terms of SPSs. These are the working formulas to calculate scattering observables in the SPS formulation.

From $f_{\nu\nu'}(k) = f_{\nu'\nu}(k)$ we obtain the reciprocity property of the scattering amplitude $f(\mathbf{k},\hat{\mathbf{r}}) = f(-k\hat{\mathbf{r}},-\hat{\mathbf{k}})$. From unitarity of the scattering matrix we obtain the optical theorem $\sigma(\mathbf{k}) = (4\pi/k)\,\mathrm{Im}\, f(\mathbf{k},\hat{\mathbf{k}})$. We also have $\sigma(\mathbf{k})|_{k\to 0} = 4\pi\alpha^2$. Let us emphasize again that all these properties hold exactly for any N and L, i.e., they hold within the SPS formulation.

IV. ILLUSTRATIVE CALCULATIONS

To illustrate the theory by calculations, we consider an anisotropic Yukawa potential

$$V(\mathbf{r}) = -\frac{e^{-\gamma R(\mathbf{r})}}{R(\mathbf{r})}, \quad R(\mathbf{r}) = \sqrt{\frac{x^2}{m_x} + \frac{y^2}{m_y} + \frac{z^2}{m_z}}. \tag{103}$$

This potential describes the interaction of an electron with an ion in an anisotropic crystal. Indeed, let $\mathbf{R} = (X,Y,Z)$ be the coordinate of the electron relative to the ion and m_x, m_y, and m_z be its effective masses for the motion in X, Y, and Z, respectively. Introducing the mass-scaled coordinates $\mathbf{r} = (x,y,z) = (\sqrt{m_x}\,X,\sqrt{m_y}\,Y,\sqrt{m_z}\,Z)$, the Schrödinger equation takes the form (1) with the potential given by Eq. (103). The exponential factor in Eq. (103) accounts for screening of the ion by other electrons. We mention that similar anisotropic Yukawa potentials are used to model the interaction between molecules in liquid crystals [70] and between colloidal platelets [71]. In the following we set $\gamma = 0.1$ and $m_z = 1$; the anisotropy of the potential is controlled by varying m_x and m_y. We consider four models to be called A, B, C, and D corresponding to the four combinations of the effective masses listed in Table I. These models exemplify spherically symmetric (A), prolate (B) and oblate (C) axially symmetric, and anisotropic (D) potentials. Although the parameters of the models may be not very realistic, they are suitable for the present illustrative purposes.

Our computational procedure generalizes the one used in Refs. [38–40] to account for the angular degrees of freedom. For the radial basis (22a) we employ a discrete variable representation basis constructed from the Legendre polynomials, as described in Ref. [38]. This basis satisfies Eqs. (20). The radial matrix elements (26a) and (26b) are calculated using the corresponding Gauss-Legendre quadrature. The angular basis (22b) is defined by Eqs. (5). The angular matrix elements (11b) are accurately calculated using appropriate Gauss-Jacobi quadratures in θ and the Gauss-Chebyshev quadrature of the first kind in φ. The SPS EVP (39) is solved using LAPACK routines [72], and this is the most time-consuming part of the calculations. Since the computational time grows as the cube of the dimension of the matrix $\mathbb{S}$ in Eq. (39), to accelerate the calculations we arrange the matrix in a block-diagonal form reflecting the symmetry of the potential, and then treat each block separately. Thus, in the spherically symmetric case (model A) both angular momentum quantum numbers l and m are conserved, and hence the blocks are labeled by $\nu = (l,m)$; in this case, each block reduces to the problem treated in

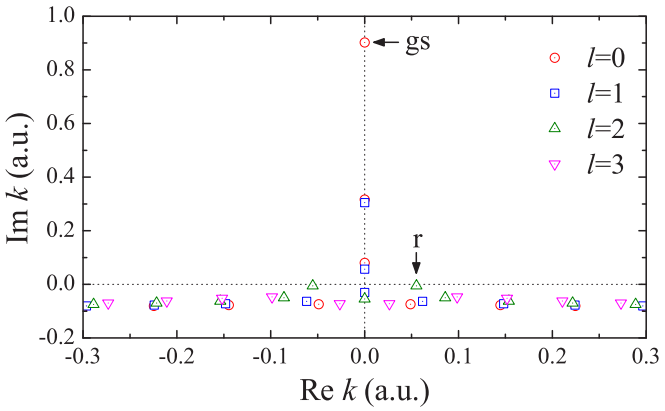

FIG. 1. SPS eigenvalues for a spherically symmetric potential (103), model A. In this case l and m are exact quantum numbers and each eigenvalue is $(2l+1)$-fold degenerate in m. The eigenvalues corresponding to different l are shown by different symbols. "gs" indicates the ground state; see Table I. "r" indicates a resonance; see Table II and Fig. 5. The results are obtained with $a = 50$ and $N = 20$.

Ref. [40]. In the axially symmetric case (models B and C) only the azimuthal quantum number m is conserved, so the blocks are labeled by m. Even in the most general anisotropic case (model D) the present potential (103) does not change under reflections $x \to -x$, $y \to -y$, and $z \to -z$, so the solutions

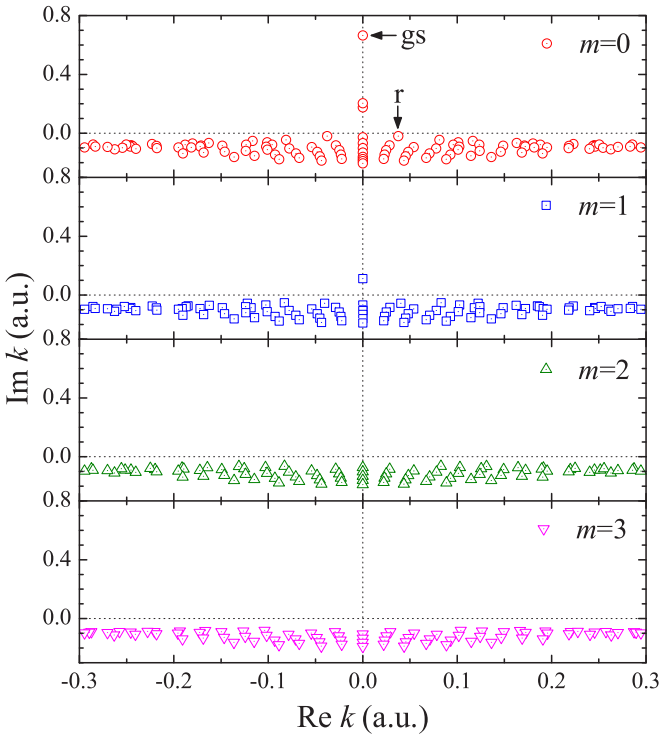

FIG. 2. SPS eigenvalues for a prolate axially symmetric potential (103), model B. In this case m is an exact quantum number and each eigenvalue for $|m| > 0$ is doubly degenerate in the sign of m. The eigenvalues corresponding to different m are shown in different panels. "gs" indicates the ground state; see Table I. "r" indicates a resonance; see Table II and Fig. 5. The results are obtained with $a = 50$, $N = 20$, and $L = 10$.

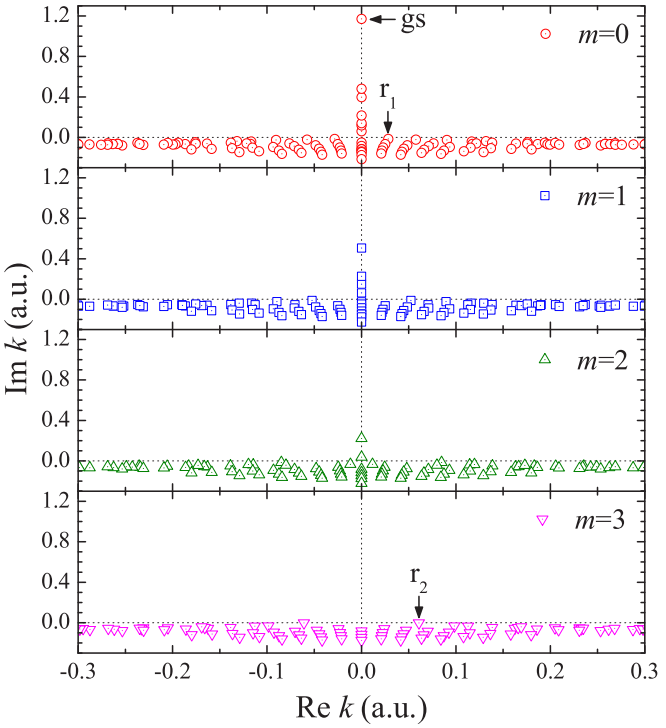

FIG. 3. Same as in Fig. 2, but for an oblate axially symmetric potential (103), model C. "gs" indicates the ground state; see Table I. "r1" and "r2" indicate two resonances; see Table II and Fig. 5. The results are obtained with $a = 50$, $N = 20$, and $L = 10$.

of Eq. (39) can be divided into eight symmetry types according to their parities with respect to these reflections. After the SPS eigenvalues $k_n = -i\lambda_n$ and surface amplitudes $\phi_{\nu n}(a) = \mathbf{f}^T \mathbf{c}_{\nu n}$ are obtained by solving Eq. (39), the scattering matrix (89) and all the other scattering characteristics can be easily calculated for any k in an interval of convergence determined by the basis. The whole computational scheme depends on three parameters: N and L, defining the dimensions of the radial and angular bases, and the cutoff radius a in Eq. (2). Convergence of the results with respect to these parameters is discussed below.

The distributions of the SPS eigenvalues k_n in the complex k plane for the four models under consideration are shown in Figs. 1–4. The eigenvalues for the spherically symmetric model A, Fig. 1, are labeled by l; for a given l, each eigenvalue is $(2l+1)$-fold degenerate in m [73]. The eigenvalues for axially symmetric models B and C, Figs. 2 and 3, are labeled by m; for a given $m \neq 0$, each eigenvalue is doubly degenerate in the sign of m. The SPSs for the anisotropic model D can be characterized by their total parity with respect to the inversion $\mathbf{r} \to -\mathbf{r}$; the eigenvalues for the even and odd states are shown separately in Fig. 4.

The eigenvalues as functions of N, L, and a behave as follows. For any given a, each eigenvalue converges as N and L grow, which simply results from completeness of the radial and angular bases. Thus, the distributions shown in Figs. 1–4 are converged with respect to N. However, even though each eigenvalue converges also with respect to L, the distributions do not. This is because new eigenvalues, representing states whose partial-wave expansion is localized at larger l, continue to appear in the regions of the complex k plane shown in

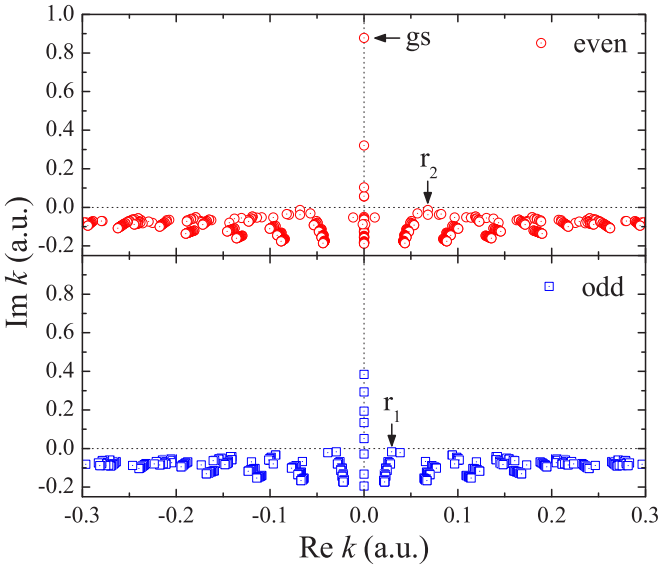

FIG. 4. SPS eigenvalues for an anisotropic potential (103), model D. In this case each state has a definite parity with respect to the inversion $\mathbf{r} \to -\mathbf{r}$. The eigenvalues corresponding to even and odd states are shown in different panels. "gs" indicates the ground state, see Table I. "r1" and "r2" indicate two resonances; see Table II and Fig. 5. The results are obtained with $a = 50$, $N = 20$, and $L = 10$.

the figures as L grows. The convergence properties of the basis-independent eigenvalues (i.e., already converged in N and L) with respect to a depend on the type of the state. Bound-state eigenvalues confidently converge as a grows, and hence can be calculated with high precision. We illustrate this for the ground state indicated in the figures by "gs". The energies of this state for the four models are given in Table I together with the minimum values of the parameters ensuring convergence of all significant digits quoted. All the other SPSs lying in the lower half of the complex k plane generally do not converge with respect to a. As a grows, they continue to move, forming sequences lying on some lines, so that their distribution along the lines becomes denser. Yet some of these SPSs may behave differently from the others, namely, although their positions continue to vary as a grows, they stay in a vicinity of some fixed point. It can be said that they converge in a, but with a limited accuracy. Such SPSs represent resonances. Several resonances are indicated in the figures; their energies and widths together with the minimum parameters ensuring convergence within the specified accuracy are given in Table II. Note that resonances converge at much larger a than bound states. For the present purely attractive potential (103) the resonances are supported by centrifugal barriers. One can see that narrow resonances satisfying conditions (67) converge to higher accuracy. But there also exist broad resonances with $\Gamma \gtrsim \mathcal{E}$, whose eigenvalues converge less convincingly. All these resonances, however, are visible in scattering characteristics (see below). Summarizing, only SPSs representing bound states and resonances, that is states observable individually, converge (resonances—to a certain extent only) with respect to all three parameters N, L, and a. All the other SPSs essentially depend on the cutoff radius a; they do not have physical meaning individually, but constitute a complete set. As will be shown shortly, scattering observables expanded in terms of this set do converge with respect to a, and this is important. All this is quite similar to the convergence properties of SPSs discussed and illustrated in Refs. [38–40].

We next discuss calculations of scattering length using Eq. (96). This requires to know only the SPS eigenvalues k_n. The results for the four models are given in Table I. While the individual eigenvalues generally do not converge with respect to a, their combination in Eq. (96) defining a physically meaningful quantity related to observables converges to high precision. Rather large values of a required for the convergence can be explained on the example of the spherically symmetric model A. In this case, the error in the value of α incurred by cutting off the tail of the potential extending beyond $r = a$ can be estimated using perturbation theory as $\delta\alpha = 2\int_a^\infty V(r)r^2\,dr \approx -2ae^{-\gamma a}/\gamma$. For $a = 240$ we obtain $|\delta\alpha| \approx 2 \times 10^{-7}$, which is consistent with the accuracy of α given in Table I. From the properties of k_n discussed in Sec. II C one can see that the first term in Eq. (96) and bound-state SPSs in the sum give positive contributions to α, while all the other SPSs together give a negative contribution. The total result can be either positive or negative, depending on the magnitudes of the contributions; our models illustrate both possibilities. If there exists a bound, antibound, or resonance state with a very small $|k_n|$, the corresponding term dominates in Eq. (96), and then α can be approximately expressed in terms of k_n for this state [1,2]. This, however, is not the case for the present models.

We now turn to scattering calculations. We restrict our consideration to low-energy scattering in the interval $0 \leqslant k \leqslant 0.3$ shown in Figs. 1–4. One reason is that in this interval the dependence of the scattering cross section on k is dominated by the resonances discussed above, so we can clearly relate scattering observables to individual SPSs. Another technical reason is that the number of partial waves required for convergence rapidly grows with k, which makes the calculations difficult. The results reported below are obtained with $N \sim 50$,

TABLE II. Energies $\mathcal{E}$ and widths Γ (in atomic units) of resonances indicated in Figs. 1–4. The sets (a,N,L) give the minimum values of the parameters for which the results converged. $x[y] = x \times 10^y$.

Model	Resonance	$\mathcal{E}$	Γ	(a,N,L)
A	r	0.151 017 960 9[−2]	0.670 188 120 7[−3]	(250,50,2)
B	r	0.447 03[−3]	0.148 670[−2]	(250,60,20)
C	r_1	0.190 625 5[−3]	0.595 970 1[−3]	(300,70,20)
C	r_2	0.180 077 752[−2]	0.437 675 76[−3]	(300,70,20)
D	r_1	0.18[−3]	0.66[−3]	(200,40,20)
D	r_2	0.226[−2]	0.199[−2]	(200,40,20)

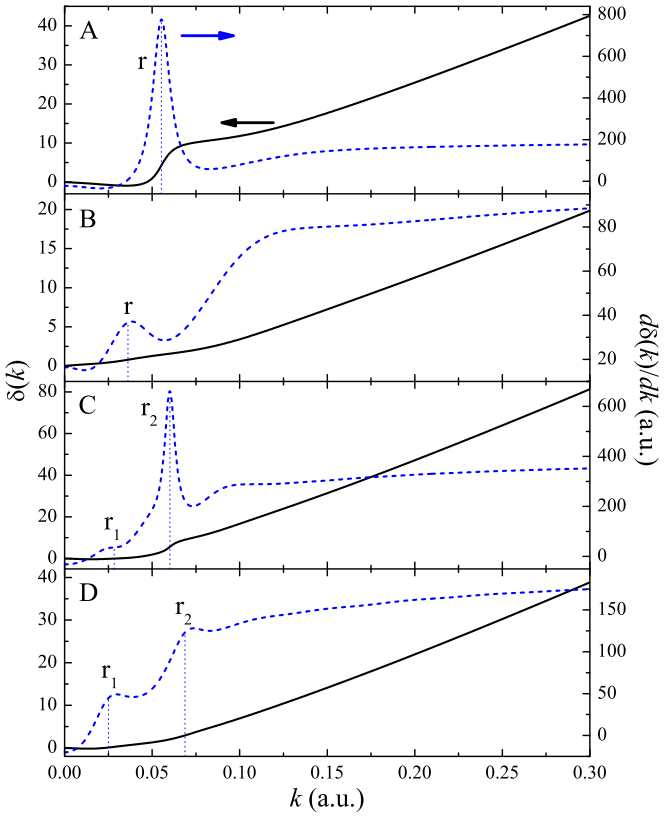

FIG. 5. Eigenphase shift sum $\delta(k)$ (solid black lines, left axis) and its derivative $d\delta(k)/dk$ (dashed blue lines, right axis) as functions of k. Panels A–D correspond to the four models whose SPS eigenvalues are shown in Figs. 1–4, respectively. The vertical dotted lines show the positions of resonances indicated in the figures and listed in Table II.

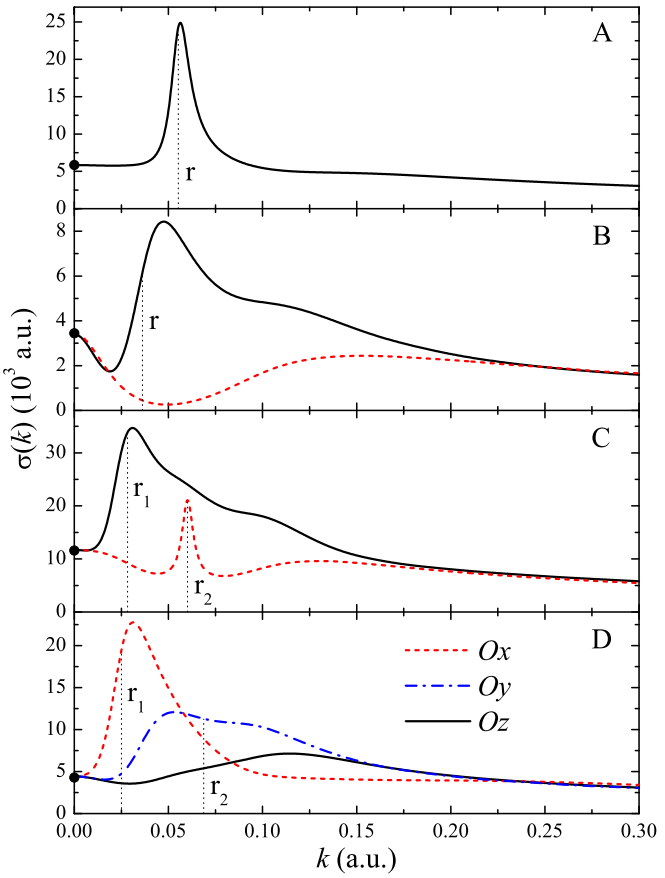

FIG. 6. Total scattering cross sections $\sigma(k)$ as functions of k for the incident momentum $\mathbf{k}$ directed along the Ox, Oy, and Oz axes. Panels A–D correspond to the four models whose SPS eigenvalues are shown in Figs. 1–4, respectively. The vertical dotted lines show the positions of resonances indicated in the figures and listed in Table II. Solid circles at $k = 0$ show the values of $4\pi\alpha^2$ with the scattering lengths from Table I.

$L \sim 20$, and $a \sim 100$ and are converged with respect to all these parameters.

We begin with the eigenphase shift sum defined by Eq. (95). It is calculated using Eq. (94), which again requires to know only the SPS eigenvalues k_n. The uncertainty in the definition of $\delta(k)$ is eliminated by the condition $\delta(0) = 0$. The results are shown by solid black lines in Fig. 5. It is well known that for spherically symmetric potentials partial-wave phase shifts rapidly grow by π as k passes through a narrow resonance [1,2]. As can be seen from Eq. (94), for general potentials the eigenphase shift sum behaves similarly. However, one should remember about possible degeneracy of the SPS eigenvalues for potentials with a symmetry. Thus, in the spherically symmetric case a resonance in a partial wave l results in the growth of $\delta(k)$ by $(2l+1)\pi$. The resonance with $l = 2$ in model A indicated in Fig. 1 by "r" is seen as a steplike structure of $\delta(k)$ in Fig. 5; the height of the step is somewhat less than 5π, because the resonance is not narrow enough. In the axially symmetric case $\delta(k)$ should grow through a resonance with $m \neq 0$ by 2π. Indeed, the resonance with $m = 3$ in model C indicated in Fig. 3 by "r_2" can be seen as a step of appropriate height in the behavior of $\delta(k)$ in Fig. 5. To make the resonances more visible, we have added to Fig. 5 plots of the derivative $d\delta(k)/dk$ shown by dashed blue lines. All resonances listed in Table II, including the broad ones with $\Gamma \gtrsim \mathcal{E}$, are clearly seen in these plots at expected positions.

The total scattering cross sections calculated using Eqs. (89), (100), and (102) are shown in Fig. 6. These calculations require to know both the SPS eigenvalues k_n and surface amplitudes $\phi_{\nu n}(a)$. For model A the cross section does not depend on the direction of the incident momentum $\mathbf{k}$, and we assume that it is directed along the Oz axis. For models B and C the cross section does not depend on the direction of the component of $\mathbf{k}$ lying in the xy plane. We consider two cases with $\mathbf{k}$ directed along the Ox and Oz axes. Finally, for model D we consider three cases with $\mathbf{k}$ directed along the Ox, Oy, and Oz axes. All resonances listed in Table II are seen in the figure. The resonance "r" in model B corresponds to $m = 0$; see Fig. 2. It reveals itself in the cross section for $\mathbf{k} \parallel Oz$, but is not seen in the cross section for $\mathbf{k} \parallel Ox$. This is explained as follows. As was mentioned above, each SPS for the present potential (103) is characterized by a signature (π_x,π_y,π_z), where $\pi_x = \pm$ is the parity with respect to the reflection $x \to -x$, and similarly for y and z. The resonance in question has signature $(+,+,-)$. This means that

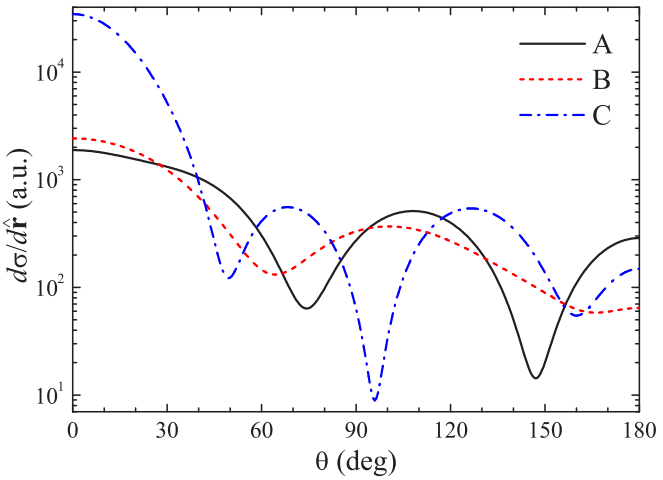

FIG. 7. Differential scattering cross sections for models A, B, and C for the incident momentum $\mathbf{k}$ directed along the Oz axis at $k = 0.1$.

its wave function is odd with respect to the reflection $z \to -z$ and turns to zero at the xy plane, and hence this SPS does not contribute to the sum in Eq. (102) for $\mathbf{k} \parallel Ox$. The same holds for the resonance "r_1" in model C; see Fig. 3. The second resonance "r_2" in model C corresponds to $m = 3$ and does not contribute to Eq. (102) for $\mathbf{k} \parallel Oz$. It is doubly degenerate and occurs with signatures $(-,+,+)$ and $(+,-,+)$; the first of these SPSs contributes to Eq. (102) for $\mathbf{k} \parallel Ox$. The resonance "r_1" in model D has signature $(-,+,+)$; it contributes to Eq. (102) for $\mathbf{k} \parallel Ox$, but does not contribute for the two other directions of $\mathbf{k}$. The second resonance "r_2" in model D has signature $(+,+,+)$ and contributes to Eq. (102) for all directions of $\mathbf{k}$. However, it is too broad and overlaps with other broad resonances, see Fig. 4, so its trace can be seen in Fig. 6 only for $\mathbf{k} \parallel Oy$. The solid circles show the values of $4\pi\alpha^2$

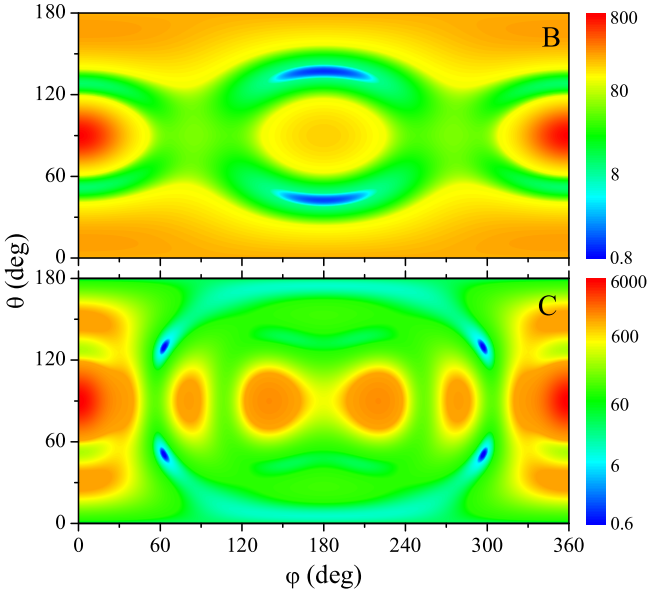

FIG. 8. Differential scattering cross sections $d\sigma/d\hat{\mathbf{r}}$ (in atomic units) for models B and C for the incident momentum $\mathbf{k}$ directed along the Ox axis at $k = 0.1$.

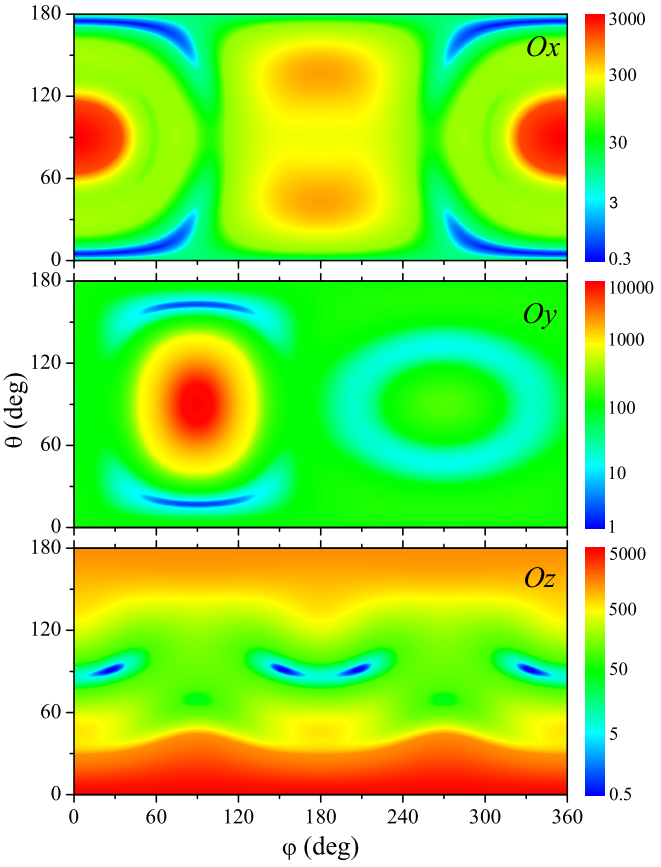

FIG. 9. Differential scattering cross sections $d\sigma/d\hat{\mathbf{r}}$ (in atomic units) for model D for the incident momentum $\mathbf{k}$ directed along the Ox, Oy, and Oz axes at $k = 0.1$.

calculated using scattering lengths given in Table I. These results are in good agreement with the values of $\sigma(k = 0)$ obtained from Eq. (102), which confirms consistency of the calculations.

We finally illustrate the calculation of the differential scattering cross section (101) using Eq. (99). We consider the same directions of the incident momentum $\mathbf{k}$ for each model as shown in Fig. 6. In all the cases, the cross section is calculated at $k = 0.1$. For models A, B, and C in the case $\mathbf{k} \parallel Oz$ the value of $d\sigma/d\hat{\mathbf{r}}$ depends only on the polar angle θ. These results are shown in Fig. 7. For models B and C in the case $\mathbf{k} \parallel Ox$ the cross section depends on both angles θ and φ defining the direction of the scattered momentum $k\hat{\mathbf{r}}$ and is symmetric with respect to the lines $\theta = \pi/2$ and $\varphi = \pi$. These results are shown in Fig. 8. For model D in the case $\mathbf{k} \parallel Ox$ the cross section is again symmetric with respect to the lines $\theta = \pi/2$ and $\varphi = \pi$, for $\mathbf{k} \parallel Oy$ it is symmetric with respect to the lines $\theta = \pi/2$ and $\varphi = \pi/2$ (φ is defined modulo 2π), and for $\mathbf{k} \parallel Oz$ it is symmetric with respect to the lines $\varphi = \pi/2$ and $\varphi = \pi$. The results for model D are shown in Fig. 9. We have verified that the optical theorem is fulfilled, which again confirms consistency of the whole approach.

V. CONCLUSIONS

The SPS formulation of scattering theory, originally developed for s-wave scattering by a central potential [38] and

then generalized to arbitrary angular momenta [40], is further generalized to arbitrary finite-range potentials without any symmetry in the 3D case. The SPS EVP (24) is linearized by extending the corresponding Hilbert space from $\mathcal{H}_{NL}$ [Eq. (33)] to $\mathcal{H}_{NL}^{\rm SPS}$ [Eq. (37)] and presented in the form (39). This enabled us to establish the fundamental orthogonality [Eqs. (47)–(50)] and completeness [Eq. (52), (54), and (55)] properties of 3D SPSs. On the basis of these relations, we have derived the SPS expansions for the outgoing-wave Green's function (79), partial-wave scattering states (87), scattering matrix (89), its determinant (94), and scattering length (96). The scattering amplitude (99) and scattering cross sections (101) and (102) are then given in terms of the scattering matrix by standard formulas [1,2]. This completes the SPS formulation of scattering theory for the present case. The theory is illustrated by calculations of bound states, resonances, scattering length, eigenphase shift sum, total, and differential scattering cross sections for several model potentials. The results confirm the power of SPSs as a universal tool for treating the whole spectrum of scattering phenomena, as was anticipated in Ref. [37].

The main virtue of the SPSs formulation is that it provides a mathematically rigorous and at the same time practical way to represent discrete and continuous spectra on an equal footing by a purely discrete set of states. An additional advantage stems from the fact that bound states and resonances, that is, all physically meaningful states observable individually, are included into the set. The efficiency of this approach was demonstrated by its applications in solving various stationary [37,42–52] and time-dependent [53–62] quantum-mechanical problems. The present work lays the foundation for extensions of the approach to more challenging problems.

ACKNOWLEDGMENT

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[1] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-relativistic Theory)* (Pergamon Press, Oxford, 1977).
[2] R. G. Newton, *Scattering Theory of Waves and Particles* (Springer-Verlag, New York, 1982).
[3] G. Breit and E. Wigner, Capture of slow neutrons, Phys. Rev. **49**, 519 (1936).
[4] A. J. F. Siegert, On the derivation of the dispersion formula for nuclear reactions, Phys. Rev. **56**, 750 (1939).
[5] G. Gamow, Zur quantentheorie des atomkernes, Z. Phys. **51**, 204 (1928).
[6] N. Hu, On the application of Heisenberg's theory of S-matrix to the problems of resonance scattering and reactions in nuclear physics, Phys. Rev. **74**, 131 (1948).
[7] J. Humblet, Sur la définition des niveaux virtuels des noyaux atomiques et l'établissement de la formule de dispersion, Mém. Soc. Roy. Sci. de Liège (8°) **12**, No. 4 (1952).
[8] T. Regge, Analytic properties of the scattering matrix, Nuovo Cimento **8**, 671 (1958).
[9] T. Regge, On the analytic behavior of the eigenvalue of the S-matrix in the complex plane of the energy, Nuovo Cimento **9**, 295 (1958).
[10] V. I. Serdobol'skiĭ, On the theory of scattering via quasi-stationary states, Zh. Eksp. Teor. Fiz. **36**, 1903 (1959) [Sov. Phys. JETP **9**, 1354 (1959)].
[11] R. E. Peierls, Complex eigenvalues in scattering theory, Proc. R. Soc. A **253**, 16 (1959).
[12] K. J. Le Couteur, The structure of a non-relativistic S-matrix, Proc. R. Soc. A **256**, 115 (1960).
[13] A. M. Dykhne and A. V. Chaplik, Normalization of the wave functions of quasistationary states, Zh. Eksp. Teor. Fiz. **40**, 1427 (1961) [Sov. Phys. JETP **13**, 1002 (1961)].
[14] Ya. B. Zel'dovich, On the theory of unstable states, Zh. Eksp. Teor. Fiz. **39**, 776 (1960) [Sov. Phys. JETP **12**, 542 (1961)].
[15] J. Humblet and L. Rosenfeld, Theory of nuclear reactions I. Resonant states and collision matrix, Nucl. Phys. **26**, 529 (1961).
[16] N. Hokkyo, A remark on the norm of the unstable state, Prog. Theor. Phys. **33**, 1116 (1965).
[17] V. S. Rudakov, On the description quasistationary states, Vestn. Leningr. Univ., Ser. 4: Fiz., Khim. **16**, 143 (1966).
[18] T. Berggren, On the use of resonant states in eigenfunction expansions of scattering and reaction amplitudes, Nucl. Phys. A **109**, 265 (1968).
[19] W. J. Romo, Inner product for resonant states and shell-model applications, Nucl. Phys. A **116**, 617 (1968).
[20] W. J. Romo, An approximation scheme for continuum shell-model calculations, Nucl. Phys. A **142**, 300 (1970).
[21] R. M. More, Perturbation of a decaying state, Phys. Rev. A **3**, 1217 (1971).
[22] R. M. More, Theory of decaying states, Phys. Rev. A **4**, 1782 (1971).
[23] É. É. Shnol, Remarks on the theory of quasistationary states, Teor. Mat. Fiz. **8**, 140 (1971) [Sov. Phys. Theor. Math. Phys. **8**, 729 (1971)].
[24] B. Gyarmati and T. Vertse, On the normalization of Gamow functions, Nucl. Phys. A **160**, 523 (1971).
[25] R. M. More and E. Gerjuoy, Properties of resonance wave functions, Phys. Rev. A **7**, 1288 (1973).
[26] D. L. Huestis, A superposition principle for Siegert resonant states, J. Math. Phys. **16**, 2148 (1975).
[27] W. J. Romo, A numerical study of resonance contributions to nuclear sum rules, Nucl. Phys. A **237**, 275 (1975).
[28] G. García-Calderón, An expansion of continuum wave functions in terms of resonant states, Nucl. Phys. A **261**, 130 (1976).
[29] W. J. Romo, A study of the convergence of Mittag-Leffler expansions of the Green function and the off-shell scattering amplitude in potential scattering, Nucl. Phys. A **302**, 61 (1978).
[30] J. Bang, F. A. Gareev, M. H. Gizzatkulov, and S. A. Goncharov, Expansion of continuum functions on resonance wave functions and amplitudes, Nucl. Phys. A **309**, 381 (1978).

[31] W. J. Romo, A study of the completeness properties of resonant states, J. Math. Phys. **21**, 311 (1980).
[32] J. Bang, S. N. Ershov, F. A. Gareev, and G. S. Kazacha, Discrete expansions of continuum wave functions, Nucl. Phys. A **339**, 89 (1980).
[33] A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, *Scattering, Reactions, and Decays in Nonrelativistic Quantum Mechanics* (Nauka, Moscow, 1971).
[34] H. M. Nussenzveig, *Causality and Dispersion Relations* (Academic Press, New York, 1972).
[35] V. I. Kukulin, V. M. Krasnopol'sky, and J. Horáček, *Theory of Resonances: Principles and Applications* (Academia, Praha, 1989).
[36] A. I. Markushevich, *Theory of Functions of a Complex Variable* (Chelsea, New York, 1985).
[37] O. I. Tolstikhin, V. N. Ostrovsky, and H. Nakamura, Siegert Pseudo-States as a Universal Tool: Resonances, *S* Matrix, Green Function, Phys. Rev. Lett. **79**, 2026 (1997).
[38] O. I. Tolstikhin, V. N. Ostrovsky, and H. Nakamura, Siegert pseudostate formulation of scattering theory: One-channel case, Phys. Rev. A **58**, 2077 (1998).
[39] G. V. Sitnikov and O. I. Tolstikhin, Siegert pseudostate formulation of scattering theory: Two-channel case, Phys. Rev. A **67**, 032714 (2003).
[40] P. A. Batishchev and O. I. Tolstikhin, Siegert pseudostate formulation of scattering theory: Nonzero angular momenta in the one-channel case, Phys. Rev. A **75**, 062704 (2007).
[41] K. Toyota, T. Morishita, and S. Watanabe, Siegert pseudostate perturbation theory: One- and two-threshold cases, Phys. Rev. A **72**, 062718 (2005).
[42] O. I. Tolstikhin, I. Yu. Tolstikhina, and C. Namba, Interference effects in the decay of resonance states in three-body Coulomb systems, Phys. Rev. A **60**, 4673 (1999).
[43] E. L. Hamilton and C. H. Greene, Competition Among Molecular Fragmentation Channels Described with Siegert Channel Pseudostates, Phys. Rev. Lett. **89**, 263003 (2002).
[44] K. Toyota and S. Watanabe, Two-channel Siegert pseudostate approach to a three-body Coulomb problem: *S*-wave resonances of $Ps^-(N = 2,3)$, Phys. Rev. A **68**, 062504 (2003).
[45] V. Kokoouline and C. H. Greene, Theory of Dissociative Recombination of D_{3h} Triatomic Ions Applied to H_3^+, Phys. Rev. Lett. **90**, 133201 (2003).
[46] G. V. Sitnikov and O. I. Tolstikhin, Quantum-mechanical and semiclassical study of the collinear three-body Coulomb problem: Resonances, Phys. Rev. A **71**, 022708 (2005).
[47] V. N. Ostrovsky and N. Elander, Scattering resonances and background associated with an asymmetric potential barrier via Siegert pseudostates, Phys. Rev. A **71**, 052707 (2005).
[48] R. Čurík and C. H. Greene, Indirect Dissociative Recombination of LiH^+ Molecules Fueled by Complex Resonance Manifolds, Phys. Rev. Lett. **98**, 173201 (2007).
[49] D. J. Haxton and C. H. Greene, *Ab initio* frame-transformation calculations of direct and indirect dissociative recombination rates of $HeH^+ + e^-$, Phys. Rev. A **79**, 022701 (2009).
[50] A. Das, E. D. Poliakoff, R. R. Lucchese, and J. D. Bozek, Mode-specific photoionization dynamics of a simple asymmetric target: OCS, J. Chem. Phys. **130**, 044302 (2009).
[51] R. Čurík and F. A. Gianturco, Indirect dissociative recombination of $LiHe^+$ ions driven by vibrational Feshbach resonances, Phys. Rev. A **87**, 012705 (2013).
[52] J. Jose and R. R. Lucchese, Vibrational effects in the shape resonant photoionization leading to the A^2T_{1u} state of SF_6^+, Chem. Phys. **447**, 64 (2015).
[53] S. Yoshida, S. Watanabe, C. O. Reinhold, and J. Burgdörfer, Reflection-free propagation of wave packets, Phys. Rev. A **60**, 1113 (1999).
[54] S. Tanabe, S. Watanabe, N. Sato, M. Matsuzawa, S. Yoshida, C. O. Reinhold, and J. Burgdörfer, Siegert-pseudostate representation of quantal time evolution: A harmonic oscillator kicked by periodic pulses, Phys. Rev. A **63**, 052721 (2001).
[55] R. Santra, J. M. Shainline, and C. H. Greene, Siegert pseudostates: Completeness and time evolution, Phys. Rev. A **71**, 032703 (2005).
[56] O. I. Tolstikhin, Siegert-state expansion for nonstationary systems: Coupled equations in the one-channel case, Phys. Rev. A **73**, 062705 (2006).
[57] O. I. Tolstikhin, Siegert-state expansion for nonstationary systems. II. The whole-axis problem, Phys. Rev. A **74**, 042719 (2006).
[58] K. Toyota, O. I. Tolstikhin, T. Morishita, and S. Watanabe, Siegert-state expansion in the Kramers-Henneberger frame: Interference substructure of above-threshold ionization peaks in the stabilization regime, Phys. Rev. A **76**, 043418 (2007).
[59] O. I. Tolstikhin, Siegert-state expansion for nonstationary systems. III. Generalized Born-Fock equations and adiabatic approximation for transitions to the continuum, Phys. Rev. A **77**, 032711 (2008).
[60] O. I. Tolstikhin, Siegert-state expansion for nonstationary systems. IV. Three-dimensional case, Phys. Rev. A **77**, 032712 (2008).
[61] K. Toyota, O. I. Tolstikhin, T. Morishita, and S. Watanabe, Interference substructure of above-threshold ionization peaks in the stabilization regime, Phys. Rev. A **78**, 033432 (2008).
[62] K. Toyota, O. I. Tolstikhin, T. Morishita, and S. Watanabe, Slow Electrons Generated by Intense High-Frequency Laser Pulses, Phys. Rev. Lett. **103**, 153003 (2009).
[63] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1957).
[64] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1963).
[65] We note that $e_l(z) = e^{i\pi(l+1)/2} z h_l^{(1)}(z)$, where $h_l^{(1)}(z)$ is a spherical Hankel function [66], but in the present analysis it is more convenient to use the explicit expression (16).
[66] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972).
[67] E. Grosswald, *Bessel Polynomials*, Lecture Notes in Mathematics No. 698) (Springer-Verlag, New York, 1978).
[68] C. Bloch, Une formulation unifiée de la théorie des réactions nucléaires, Nucl. Phys. **4**, 503 (1957).
[69] F. R. Gantmacher, *The Theory of Matrices* (AMS Chelsea, Providence, 2000). The authors of Ref. [38] were not aware of this powerful result, which explains the need of Appendix A therein.

[70] M. Holovko, D. di Caprio, and I. Kravtsiv, Maier-Saupe nematogenic fluid: field theoretical approach, Condens. Matter Phys. **14**, 33605 (2011).

[71] S. Jabbari-Farouji, J.-J. Weis, P. Davidson, P. Levitz, and E. Trizac, Interplay of anisotropy in shape and interactions in charged platelet suspensions, J. Chem. Phys. **141**, 224510 (2014).

[72] LAPACK, Linear algebra package, http://www.netlib.org/lapack/.

[73] One can notice that in arriving at Eq. (47) we assumed that all the SPS eigenvalues are distinct. In the presence of an exact symmetry of the potential, when the matrix $\mathbb{S}$ in Eq. (39) has block-diagonal form, it is sufficient to require that all eigenvalues of the same symmetry block are distinct.