Positive energy Sturmian states for two-Coulomb-center problems

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Properties of two-center Coulomb Sturmian basis sets are discussed. Analytic and numerical techniques to calculate these functions and coupling matrix elements are developed. A class of Sturmian functions is found that has no analytic continuation to negative energies and is not present in one-center potentials. Advantages of Sturmian sets over conventional eigenstate sets are emphasized. [S1050-2947(97)06205-7]

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I. INTRODUCTION

Most basis-set representations of wave functions for quantum systems employ energy eigenstates of some model Hamiltonian. Sturmian representations are exceptional in this regard since the Sturmian eigenfunctions are not energy eigenstates. Here we employ the nomenclature that has become conventional in the physics literature, namely, eigenfunctions of a Schrödinger equation, where the energy is fixed and the coefficient of the potential is the eigenvalue, are called Sturmian eigenfunctions.

The advantages of Sturmian basis sets can be summarized as follows. (i) Sturmian basis sets are complete and square integrable for negative energies. (ii) Sturmians functions can be *defined* to satisfy appropriate physical boundary conditions, e.g., bound-state boundary conditions for bound states and outgoing (or incoming) boundary conditions at positive energies. (iii) Sturmian functions diagonalize the potential and therefore are superior to energy eigenstates for representing waves in regions where the potential is strongest. In other words, all Sturmian functions with a fixed energy are well localized in the physically relevant region of the potential. For this reason they often provide rapidly convergent expansions of wave functions for complex systems. (iv) Superior localization of Sturmian basis sets can be effectively employed to describe dynamic atomic and molecular systems characterized by the electronic states that are initially known to be localized around one particular center of force. This property can be especially useful when describing atomic collisions.

Despite their attractive features, these functions are not widely used. Most applications exploit elementary properties of these states, namely, completeness and square integrability for negative energy [1]. Use of outgoing wave Sturmian functions in nuclear physics has been reviewed by Rawitscher [2], and Shakeshaft [3] has discussed outgoing-wave Sturmian functions for one-center Coulomb potentials. Shakeshaft has shown that more familiar negative energy Sturmians can be analytically continued to positive energies, where they represent outgoing waves.

In all of these cases Sturmian functions were defined for a simple central potential $V(r)$. Little is known about Sturmian functions for more complicated potentials. Recently, Sturmian functions for the two-center Coulomb potential have been employed to study ion-atom collisions [4]. Positive energy Sturmian functions were needed to represent ionization in such collisions. In this paper we consider the properties of two-center Sturmian functions and compare them with more familiar Sturmian functions for central Coulomb potentials.

In Sec. II we review the standard Sturm-Liouville theory on a finite interval and then consider Sturmian functions on semi-infinite intervals, which are much more relevant in physical applications. The properties of Sturmian sets are compared with sets of conventional energy eigenstates, and then we present a practical example of a one-center Coulomb set.

Analytic and numerical techniques to calculate the Sturmian functions for two-center Coulomb potentials are described in Sec. III. One of the remarkable features of these Sturmian functions is the existence of a class of positive energy Sturmians having no analytic continuation to negative energy. This very interesting property has no analog in the one-center case. In Sec. III we present methods of matrix element calculations using the Sturmian functions for two-center Coulomb potentials. These matrix elements have been employed in Ref. [4] to calculate the spectra of electrons ejected in atomic collisions with very broad ranges of relative velocities. Atomic units are used throughout.

II. REVIEW OF STURMIAN THEORY

A. One-dimensional space

1. Sturmian theory on finite intervals

A Sturm-Liouville problem [5] is furnished by the following differential system with two-point boundary conditions:

$$[H_0(q)+\rho_\nu V(q)-\omega]S_\nu(\omega;q)=0, \tag{2.1}$$

$$\left.\frac{\partial S_\nu(\omega;q)}{\partial q}\right|_{q=a}+\alpha S_\nu(\omega;a)=0, \tag{2.2}$$

$$\left.\frac{\partial S_\nu(\omega;q)}{\partial q}\right|_{q=b}-\beta S_\nu(\omega;b)=0, \tag{2.3}$$

where

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$$H_0(q) = -\frac{1}{2}\left[K_1(q)^{-1} \frac{d}{dq} K_1(q) \frac{d}{dq} + K_2(q) \right]. \quad (2.4)$$

Hamiltonians of the form H_0 often result from variable separation of the Laplace equation in curvilinear coordinates. Reflecting wall $S_\nu(\omega;a)=0$ and ''zero momentum'' $\partial S_\nu(\omega;q)/\partial q|_{q=a}=0$ boundary conditions are special cases of the homogeneous conditions, Eqs. (2.2) and (2.3), which correspond to $\alpha=\infty$ and $\alpha=0$, respectively.

We assume that $V(q)$, $K_1(q)$, and $K_2(q)$ are real piecewise-continuous functions of q on the interval $a \leqslant q \leqslant b$, are independent of ρ, and $V(q)$ is of one sign throughout this interval. The coefficients α and β and the constant ω can be complex. Then there exists an infinite set of eigenvalues $\rho_\nu = \rho_\nu(\omega)$, $\nu = 0,1,2 \ldots$, which has no limit points, except for $\rho=\infty$. The corresponding Sturmian eigenfunctions $S_\nu(\omega;q) = \langle q|S_\nu(\omega)\rangle$ have exactly ν zeros in the interval $a \leqslant q \leqslant b$ and form a complete set on this interval with the closure property

$$\sum_\nu S_\nu(\omega;q) S_\nu(\omega;q') = -\delta(q-q')/V(q). \quad (2.5)$$

Sturmian eigenfunctions are normalized according to

$$\langle S_\nu(\omega)|-V|S_{\nu'}(\omega)\rangle = -\int_a^b S_\nu(\omega;q) V(q) S_{\nu'}(\omega;q)\,dq = \delta_{\nu\nu'}. \quad (2.6)$$

Note that dual functions $\langle S_\nu(\omega)|$ are defined as $\langle S_\nu(\omega)|\mathbf{q}\rangle = S_\nu(\omega;\mathbf{q})$, and we do not take the complex conjugate of $S_\nu(\omega;\mathbf{q})$ in Eq. (2.6). The potential is diagonal in the Sturmian representation. The Sturmian functions are normalized by Eq. (2.6) so that the diagonal matrix elements equal -1. This choice for the normalization constant is employed since the potentials $V(q)$ of interest are usually negative definite. Normalizing the Sturmian potential matrix to -1 ensures that the Sturmian functions are real for real negative energies ω and real constants α,β.

Contrary to energy eigenstate representations, the overlap matrix element in the Sturmian representation is not diagonal. Since both the normalization and overlap matrix elements are needed in practical applications, methods to compute these quantities for two-center Coulomb Sturmian functions are presented in Sec. III.

Familiar energy eigenstate basis functions of the Hamiltonian $H_0(q)$ are particular cases of Sturm-Liouville eigenfunctions when $V(q)=-1$ and $\omega=0$. As will be seen below such a correspondence between Sturmian and energy eigenstates bases can be established only on a finite interval.

2. Sturmian theory on semi-infinite intervals

In physical applications Sturm-Liouville problems on semi-infinite intervals (a is finite and $b\to\infty$), with functions $V(q)$ and $K_2(q)$ vanishing at infinity as $1/q$ or faster, are common. In this case the boundary condition, Eq. (2.3), is

$$\frac{\partial S(\omega;q)}{\partial q} + \kappa S(\omega;q) \sim 0 \quad \text{as } q\to\infty. \quad (2.7)$$

Because Eq. (2.7) must be satisfied at successive point q, it follows from Eq. (2.1) that $S(\omega;q) \propto \exp(-\kappa q)$ at large q. For real and negative ω the differential equation (2.1) gives $\kappa = \sqrt{-2\omega}$ and the boundary condition (2.7) is equivalent to $S_\nu(\omega;q)\sim 0$ as $q\to\infty$. The Sturmian functions $S_\nu(\omega)$ form a complete set in the space L_V of all piecewise-continuous functions $f(q)=\langle q|f\rangle$ having finite matrix elements $\langle f|V|f\rangle$.

Sturmian and eigenstate problems differ significantly on semi-infinite intervals because the assumption $V(q)\to 0$ as $q\to\infty$ contradicts $V(q)=-1$, which we used at the end of Sec. II A 1 to transform Sturm-Liouville problems (2.1)–(2.3) into eigenstate problems

$$H_0(q)\varphi_\nu(q) = \varepsilon_\nu \varphi_\nu(q), \quad \varphi_\nu(a)=0, \quad \varphi_\nu(q)\sim 0 \quad \text{as } q\to\infty. \quad (2.8)$$

Energy eigenfunctions for $\varepsilon_\nu<0$ do not form a complete set. For a $K_2(q)<0$ that vanishes faster than $1/q^2$ there is a finite number of eigenstates, and if $K_2(q)<0$ vanishes as $1/q^k$ with $1\leqslant k\leqslant 2$ then there is an infinite number of eigenvalues ε_ν ($n=0,1,2\ldots$) with a limit point $\lim_{n\to\infty}\varepsilon_\nu = 0$. In either case a complete set of eigenstates includes both discrete ($\varepsilon_\nu<0$) and continuum states ($\varepsilon>0$). The continuum eigenstates are not related to Sturm-Liouville problems since their asymptotic properties are determined completely by the Schrödinger equation (2.1) and cannot be chosen *a priori*.

As far as Sturmians functions are concerned, one is free to choose a basis set with an asymptotic behavior that is most suitable in a particular physical situation. Thus, for $\omega>0$ we define two complex conjugate sets of Sturmian functions. (i) Outgoing Sturmian functions satisfying outgoing-wave boundary conditions are obtained by analytic continuation of the boundary conditions (2.7) with $\kappa\to -ip$ ($p=\sqrt{2\omega}$),

$$\frac{\partial S_\nu^{\text{out}}(\omega;q)}{\partial q} - ip S_\nu^{\text{out}}(\omega;q) \sim 0 \quad \text{as } q\to\infty. \quad (2.9)$$

(ii) Incoming Sturmian functions satisfying incoming wave boundary conditions

$$\frac{\partial S_\nu^{\text{in}}(\omega;q)}{\partial q} + ip S_\nu^{\text{in}}(\omega;q) \to 0 \quad \text{as } q\to\infty \quad (2.10)$$

are obtained by analytic continuation to $\omega>0$ of the boundary conditions (2.7), with $\kappa\to ip$. For real ω these two sets of Sturmian functions are complex conjugate $\rho_\nu^{\text{in}}(\omega) = [\rho_\nu^{\text{out}}(\omega)]^*$ and $S_\nu^{\text{in}}(\omega;q) = [S_\nu^{\text{out}}(\omega;q)]^*$.

Notice that both incoming and outgoing Sturmian functions at positive ω are analytic continuations of the same set of Sturmian functions at negative ω. For this reason standing-wave boundary conditions cannot be used for Sturmian functions on semi-infinite intervals.

For short-range potentials [when $V(q)$ and $K_2(q)$ vanish at infinity faster than $1/q$] the matrix elements $\langle S_\nu^{\text{in}}(\omega)|-V|S_{\nu'}^{\text{out}}(\omega)\rangle$ are finite and both sets remain complete in the space L_V as $b\to\infty$ (see Appendix A). This means that incoming waves can be expanded in terms of outgoing Sturmian functions. But from the physical point of view it is desirable to expand incoming waves in terms of incoming

Sturmian functions and outgoing waves in terms of outgoing Sturmian functions. If $V(q)$ vanishes at infinity as $1/q$, the set of outgoing Sturmian functions is complete in the space $L_V^{\rm out}$ of all piecewise continuous functions $f(q)$ from L_V with asymptotic behavior $f \propto q^{\gamma}\exp(ipq)$ at $q\to\infty$, where $p\geqslant 0$.

B. Matrix elements

The matrix elements $M_{\nu\nu'}(\omega,\omega')=\langle S_\nu^{\rm out}(\omega)|S_{\nu'}^{\rm out}(\omega')\rangle$ and $\mathcal{M}_{\nu\nu'}(\omega,\omega')=\langle S_\nu^{\rm in}(\omega)|S_{\nu'}^{\rm out}(\omega')\rangle$ are important in physical applications. Using the definition of Sturmian functions (2.1), it is easy to show that, if $\omega\neq\omega'$, then

$$M_{\nu\nu'}(\omega,\omega')=\frac{\rho_\nu^{\rm out}(\omega)-\rho_{\nu'}^{\rm out}(\omega')}{\omega-\omega'}\langle S_\nu^{\rm out}(\omega)|-V|S_{\nu'}^{\rm out}(\omega')\rangle,$$

$$\mathcal{M}_{\nu\nu'}(\omega,\omega')=\frac{\rho_\nu^{\rm in}(\omega)-\rho_{\nu'}^{\rm out}(\omega')}{\omega-\omega'}\langle S_\nu^{\rm in}(\omega)|-V|S_{\nu'}^{\rm out}(\omega')\rangle. \tag{2.11}$$

The matrix elements

$$M_{\nu\nu'}(\omega)\equiv M_{\nu\nu'}(\omega,\omega)=\langle S_\nu^{\rm out}(\omega)|S_{\nu'}^{\rm out}(\omega)\rangle \tag{2.12}$$

are of special interest since they couple different Sturmian states in physical problems. Using the obvious equality

$$\left\langle S_\nu^{\rm out}(\omega)\left|\frac{\partial}{\partial\omega}[H_0(q)+\rho_\nu^{\rm out}V(q)-\omega]\right|S_{\nu'}^{\rm out}(\omega)\right\rangle=0,$$

the Sturmian eigenvalue equations (2.1) and orthonormality conditions, (2.6), it is easy to show that

$$M_{\nu\nu'}(\omega)=\left\langle S_\nu^{\rm out}(\omega)\left|-V\frac{\partial}{\partial\omega}\right|S_{\nu'}^{\rm out}(\omega)\right\rangle[\rho_\nu^{\rm out}(\omega)-\rho_{\nu'}^{\rm out}(\omega)] - \delta_{\nu\nu'}\frac{d\rho_\nu^{\rm out}(\omega)}{d\omega}. \tag{2.13}$$

Since the matrix elements are symmetric $M_{\nu'\nu}(\omega)=M_{\nu\nu'}(\omega)$, coupling matrix elements $\langle S_\nu(\omega)|-V|(\partial/\partial\omega)S_{\nu'}(\omega)\rangle$ are antisymmetric and the diagonal coupling matrix elements are equal to zero. If V is either a Coulomb potential or a harmonic-oscillator potential, then $M_{\nu'\nu}(\omega)$ is a tridiagonal matrix.

The matrix elements $\mathcal{M}_{\nu\nu'}(\omega,\omega')$ have a pole at $\omega=\omega'$ and, if the $\langle S_\nu^{\rm in}(\omega)|-V|S_{\nu'}^{\rm out}(\omega)\rangle$ are finite, then the pole is of the first order with residue

$$R_{\nu\nu'}(\omega)\equiv \operatorname*{Res}_{\omega\to\omega'}\mathcal{M}_{\nu\nu'}(\omega,\omega') =[\rho_\nu^{\rm in}(\omega)-\rho_{\nu'}^{\rm out}(\omega)]\langle S_\nu^{\rm in}(\omega)|-V|S_{\nu'}^{\rm out}(\omega)\rangle. \tag{2.14}$$

The expansion of incoming Sturmian functions in terms of outgoing Sturmian functions is then

$$S_\nu^{\rm in}(\omega,q)=\sum_{\nu'}\frac{R_{\nu\nu'}(\omega)}{\rho_{\nu'}^{\rm in}(\omega)-\rho_\nu^{\rm out}(\omega)}S_{\nu'}^{\rm out}(\omega,q), \tag{2.15}$$

which converges, but not absolutely.

C. Three-dimensional space

In three-dimensional cases, which we will consider further, we have

$$[H_0(\mathbf{q})+\rho_\nu V(\mathbf{q})]S_\nu^{\rm out}(\omega;\mathbf{q})=\omega S_\nu^{\rm out}(\omega;\mathbf{q}), \tag{2.16}$$

where

$$H_0(\mathbf{q})=-\frac{1}{2}\nabla_{\mathbf{q}}^2.$$

We also impose outgoing wave boundary conditions

$$\frac{\partial S_\nu^{\rm out}(\omega;\mathbf{q})}{\partial q}-ipS_\nu^{\rm out}(\omega;\mathbf{q})\sim 0 \quad \text{as} \quad q\to\infty \tag{2.17}$$

and require that Sturmian functions $S(\omega;\mathbf{q})$ be regular at all $\mathbf{q}$. Normalization conditions, in this case, have the form

$$-\int S_\nu(\omega;\mathbf{q})V(q)S_{\nu'}(\omega;\mathbf{q})d^3q=\delta_{\nu\nu'}. \tag{2.18}$$

III. TWO-COULOMB-CENTER STURMIANS

A. Sturmian eigenvalues

1. Calculation of Sturmian eigenvalues

Consider the time-independent Schrödinger equation of two Coulomb centers

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}\right)\varphi_\nu(R;\mathbf{r})=E_\nu(R)\varphi_\nu(R;\mathbf{r}), \tag{3.1}$$

where $r_1=|\mathbf{r}-\mathbf{R}/2|$, $r_2=|\mathbf{r}+\mathbf{R}/2|$, and R is the distance between two centers. Introducing the scaled variables $\mathbf{q}=\mathbf{r}/R$, we obtain Eq. (3.1) in the form

$$\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2+R\left(-\frac{Z_1}{q_1}-\frac{Z_2}{q_2}\right)\right]\varphi_\nu(R;\mathbf{q})=E_\nu(R)R^2\varphi_\nu(R;\mathbf{q}), \tag{3.2}$$

where $q_i=r_i/R$.

The Sturmian basis set is defined by

$$\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2+\rho_\nu\left(-\frac{Z_1}{q_1}-\frac{Z_2}{q_2}\right)\right]S_\nu(\omega;\mathbf{q})=\omega S_\nu(\omega;\mathbf{q}). \tag{3.3}$$

It is known [7] that an infinite set of adiabatic eigenvalues $E_\nu(R)$ represents different sheets of the same analytic function $\varepsilon(R)$ on a multisheeted Riemann surface. A comparison of Eqs. (3.2) and (3.3) shows that the Sturmian eigenvalues are solutions of the equation

$$E(\rho)\rho^2=\omega. \tag{3.4}$$

It follows that the Sturmian eigenfunctions $S_\nu(\omega;\mathbf{q})$ are proportional to the adiabatic functions at $R=\rho_\nu(\omega)$.

Following the work of Solov'ev [8], which was in its turn based on the work of Komarov *et al.* [9], we obtain an

algorithm for calculating the Sturmian eigenvalues. Using prolate spheroidal coordinates defined by

$$\xi=q_1+q_2, \quad \eta=q_1-q_2, \quad \phi=\arctan\left(\frac{x}{y}\right),$$

$$1\leqslant\xi<\infty, \quad -1\leqslant\eta\leqslant 1, \quad 0\leqslant\phi<2\pi,$$

where x and y are the Cartesian coordinates, and substituting the wave function

$$S(\omega;\mathbf{q})=A(\omega)G(\xi)F(\eta)\exp(im\phi) \tag{3.5}$$

into Eq. (3.1), gives the set of differential equations

$$\left[\frac{1}{\xi^2-1}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}-\frac{\lambda_\xi}{\xi^2-1}+\frac{\omega}{2}+\rho\frac{(Z_1+Z_2)\xi}{\xi^2-1}-\frac{m^2}{(\xi^2-1)^2}\right]G(\xi)=0, \tag{3.6}$$

$$\left[\frac{1}{1-\eta^2}\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta}+\frac{\lambda_\eta}{1-\eta^2}+\frac{\omega}{2}+\rho\frac{(Z_1-Z_2)\eta}{1-\eta^2}-\frac{m^2}{(1-\eta^2)^2}\right]F(\eta)=0, \tag{3.7}$$

where $A(\omega)$ is a normalization factor and λ is a separation constant. Upon choosing the expansions

$$G(\xi)=\left(\frac{\xi+1}{2}\right)^{\sigma-1}e^{i\sqrt{2\omega}(\xi-1)/2}\sum_{s=0}^{\infty}g_s\left(\frac{\xi-1}{\xi+1}\right)^{s+m/2}, \tag{3.8}$$

$$F(\eta)=e^{i\sqrt{2\omega}(1+\eta)/2}\sum_{s=0}^{\infty}c_sP_{s+m}^{(m)}(\eta), \tag{3.9}$$

where

$$\sigma=-i\frac{\rho(Z_1+Z_2)}{\sqrt{2\omega}} \tag{3.10}$$

and $P_{s+m}^{(m)}(x)$ are the associated Legendre polynomials, the differential equations (3.6) and (3.7) can be replaced by recursion relations for the coefficients g_s and c_s

$$\alpha_sg_{s+1}-\beta_sg_s+\gamma_sg_{s-1}=0, \tag{3.11}$$

$$\rho_sc_{s+1}-\chi_sc_s+\delta_sc_{s-1}=0, \tag{3.12}$$

with

$$\alpha_s=(s+1)(s+m+1), \tag{3.13}$$

$$\beta_s=2s(s+m+1-i\sqrt{2\omega}-\sigma)-(\sigma-1)(m+1)+i\sqrt{2\omega}(\sigma-m-1)+\lambda_\xi, \tag{3.14}$$

$$\gamma_s=(s+m-\sigma)(s-\sigma), \tag{3.15}$$

$$\rho_s=\frac{(s+2m+1)[\rho(Z_1-Z_2)+i\sqrt{2\omega}(s+m+1)]}{2(s+m)+3}, \tag{3.16}$$

$$\chi_s=(s+m)(s+m+1)-\lambda_\eta, \tag{3.17}$$

$$\delta_s=\frac{s[\rho(Z_1-Z_2)-i\sqrt{2\omega}(s+m)]}{2(s+m)-1}. \tag{3.18}$$

We impose the boundary conditions

$$|G(\pm1)|<\infty, \quad |F(1)|<\infty, \quad F(\xi)+\frac{i}{\sqrt{2\omega}}\frac{\partial F(\xi)}{\partial\xi}\underset{\xi\to\infty}{\to}0, \tag{3.19}$$

which implies that the expansion terminates for negative s values, i.e.,

$$g_{-1}=0, \quad c_{-1}=0. \tag{3.20}$$

Then we find that for large s, g_s, and c_s we have the asymptotic forms

$$g_s=(-1)^s\exp[-2(8\omega)^{1/4}\sqrt{is}], \tag{3.21}$$

$$c_s=\left(\frac{\omega}{2}\right)^{s/2}\frac{i^s}{s!}. \tag{3.22}$$

The recursion equations (3.11) and (3.12) can be written as infinite continued fractions $D_\xi=g_{-1}/g_\infty$ and $D_\eta=c_{-1}/c_\infty$,

$$D_\xi(\lambda,\rho,\omega)=-\frac{1}{\gamma_0}\left(\beta_0-\frac{\alpha_0\gamma_1}{\beta_1-}\frac{\alpha_1\gamma_2}{\beta_2-}\frac{\alpha_2\gamma_3}{\beta_3-}\cdots\right), \tag{3.23}$$

$$D_\eta(\lambda,\rho,\omega)=-\frac{1}{\delta_0}\left(\chi_0-\frac{\rho_0\delta_1}{\chi_1-}\frac{\rho_1\delta_2}{\chi_2-}\frac{\rho_2\delta_3}{\chi_3-}\cdots\right). \tag{3.24}$$

Finally, taking into account the boundary condition (3.19) and the restriction (3.20), we obtain two transcendental equations

$$D_\xi(\lambda_\xi,\rho,\omega)=0, \tag{3.25}$$

$$D_\eta(\lambda_\eta,\rho,\omega)=0. \tag{3.26}$$

Equations (3.25) and (3.26) are solved for $\lambda_\xi=\lambda_\xi(\rho,\omega)$ and $\lambda_\eta=\lambda_\eta(\rho,\omega)$, respectively. The Sturmian eigenvalues $\rho_\nu(\omega)$ are then calculated to any desired accuracy by solving the equation

$$\lambda_\xi(\rho,\omega)=\lambda_\eta(\rho,\omega) \tag{3.27}$$

numerically, using the properties of continued fractions [6].

When $Z_1=Z_2$ Eqs. (3.25) and (3.26) are uncoupled since $D_\eta(\lambda,\omega)$ is independent of ρ. In this case we determine $\lambda_\eta=\lambda_\eta(\omega)$ from, the now real, Eq. (3.26) and substitute $\lambda_\eta(\omega)$ into Eq. (3.25), obtaining $D_\xi(\lambda_\eta(\omega),\rho,\omega)=0$. The roots of this are eigenvalues $\rho_\nu=\rho_\nu(\omega)$.

B. Wave functions and matrix elements

1. Quasiangular wave functions

For convenience, in the calculations of matrix elements we use an alternative expansion of $G(\eta)$ in Eq. (3.7):

$$F(\eta)\frac{e^{im\phi}}{\sqrt{2\pi}}=\sum_{s=m}^{\infty} f_s Y_{lm}(\eta,\phi), \tag{3.28}$$

where $Y_{lm}(\eta,\phi)$ are spherical harmonics. Truncating the expansion (3.28) ($s=m,\ldots,K_\eta$), we calculate the eigenvector $\mathbf{f}=[f_m f_{m+1}\cdots f_{K_\eta}]$ corresponding to the eigenvalue λ_ν as a solution of the matrix equation

$$\underline{\mathcal{F}}\,\mathbf{f}=\lambda_\nu \underline{I}\mathbf{f}, \tag{3.29}$$

where $\underline{I}$ is a unit $(K_\eta-m+1)$-dimensional matrix and $\underline{\mathcal{F}}$ is a symmetric $(K_\eta-m+1)$-dimensional matrix, of which the nonvanishing matrix elements are

$$\mathcal{F}_{s,s}=-s(s+1)+\frac{\omega}{2}-\frac{\omega}{2}\left(\frac{2s^2+2s-2m^2-1}{(2s+3)(2s-1)}\right),$$

$$\mathcal{F}_{s,s+1}=\mathcal{F}_{s+1,s}=-\rho_\nu(Z_1-Z_2)\sqrt{\frac{(s+m+1)(s-m+1)}{(2s+1)(2s+3)}},$$

$$\mathcal{F}_{s,s+2}=\mathcal{F}_{s+2,s}=-\frac{\omega}{2(2s+3)}\times\sqrt{\frac{(s+m+1)(s-m+1)(s+m+2)(s-m+2)}{(2s+1)(2s+5)}}. \tag{3.30}$$

For $Z_1\neq Z_2$ the matrix $\underline{\mathcal{F}}$ is a pentadiagonal matrix. Obviously, for the case $(Z_1=Z_2)$, the off-diagonal matrix elements $\mathcal{F}_{s,s+1}$ vanish [Eq. (3.30)]. The matrix $\underline{\mathcal{F}}$ can be telescoped to an effective tridiagonal matrix by an appropriate relabeling of its elements. We normalize the vector $\mathbf{f}$ by the condition

$$\int_{-1}^{1} F^2(\eta)\,d\eta=1, \tag{3.31}$$

which is equivalent to

$$\sum_{s=m}^{K_\eta} f_s^2=1. \tag{3.32}$$

2. Quasiradial wave functions

The matrix equation related to Eq. (3.6), when we truncate the expansion (3.8) ($s=0,\ldots,K_\xi$), has the form

$$\underline{\mathcal{G}}\mathbf{g}=\lambda_\nu \underline{I}\mathbf{g}, \tag{3.33}$$

where $\mathbf{g}=[g_0 g_1\cdots g_{K_\xi}]$ is a $(K_\xi+1)$-dimensional vector and $\underline{\mathcal{G}}$ is a tridiagonal $(K_\xi+1)$-dimensional matrix, the nonvanishing matrix elements of which are

$$\mathcal{G}_{s,s}=2s(s+m+1-i\sqrt{2\omega}-\sigma)-(\sigma-1)(m+1)+i\sqrt{2\omega}(\sigma-m-1),$$

$$\mathcal{G}_{s,s+1}=(s+1)(s+m+1),$$

$$\mathcal{G}_{s+1,s}=(s+1-\sigma)(s+m+1-\sigma). \tag{3.34}$$

The vector $\mathbf{g}$ is normalized by the condition

$$\int_1^\infty G^2(\xi)\,d\xi=1. \tag{3.35}$$

Inserting the expansion (3.9) into Eq. (3.35) and making the substitution $\xi=2t-1$ we obtain

$$2\sum_{k=0}^{K_\xi} I_{k+m}(2\sigma,2\sqrt{2\omega})B_k=1,$$

$$I_k(a,x)=\int_1^\infty t^{a-2}\left(\frac{t-1}{t}\right)^k e^{ix(t-1)}dt=k!\,U(k+1,a,-ix),$$

$$B_k=\sum_{s=0}^{k} g_s g_{k-s}, \tag{3.36}$$

where $U(a,b,z)$ is the confluent hypergeometric function [6]. If $a=k+2$, then

$$I_k(k+2,x)=(ix)^{-k-1}k!,$$

$$I_{k+1}(k+2,x)=(k+1)!\;e^{-ix}\Gamma(-k-1,-ix), \tag{3.37}$$

otherwise, to evaluate the integrals $I_k(a,x)$, it is convenient to use the recurrence formula

$$I_{k+1}(a,x)=\frac{1}{k+2-a}[(2k+2-a-ix)I_k(a,x)-kI_{k-1}(a,x)], \tag{3.38}$$

which enables us to reduce the integrals $I_k(a,x)$ to the integrals with $k=0$ and $k=1$

$$I_1(a,x)=\frac{1}{2-a}[(2-a-ix)I_0(a,x)-1],$$

$$I_0(a,x)=e^{-ix}(-ix)^{1-a}\Gamma(a-1,-ix), \tag{3.39}$$

where $\Gamma(a,z)$ is the incomplete Gamma functions [6]. We find that for large k, $I_k(a,x)$ has the asymptotic form:

$$I_k(a,x)\approx\exp(-2\sqrt{ixk}) \tag{3.40}$$

and, if $x>0$, converges as $k\to\infty$.

3. Normalization factors

To determine the normalization factor in Eq. (3.5), we consider the Sturmian normalization relation [Eq. (2.18)], which, after substituting

$$V=-2\frac{(Z_1+Z_2)\xi+(Z_1-Z_2)\eta}{\xi^2-\eta^2},$$

$$d^3q=\frac{1}{8}(\xi^2-\eta^2)d\xi\, d\eta d\phi$$

and integrating over ϕ, becomes

$$\frac{1}{4}A_\nu^2(\omega)\int_1^\infty\int_{-1}^1[(Z_1+Z_2)\xi + (Z_1-Z_2)\eta]G_\nu^2(\xi)F_\nu^2(\eta)d\xi\, d\eta=1. \tag{3.41}$$

Taking into account Hellman-Feynmann properties [Eqs. (B1) and (B3)] we obtain

$$A^2(\omega)=4\left(\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\rho}-\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\rho}\right)^{-1} =4\frac{d\rho}{d\omega}\left(\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\omega}-\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\omega}\right)^{-1}. \tag{3.42}$$

The asymptotic form of the wave functions at large q is

$$S_\nu(\mathbf{q})\sim C_\nu(\omega)q^{\sigma_\nu-1}e^{i\sqrt{2\omega}q}F_\nu(\cos\theta)\exp(im\phi), \tag{3.43}$$

where

$$C_\nu(\omega)=A_\nu(\omega)e^{-i\sqrt{\omega/2}}\sum_{s=0}^{K_\xi}g_s. \tag{3.44}$$

4. Orthogonality

The orthogonality relations have the form

$$\frac{1}{4}A_\nu(\omega)A_{\nu'}(\omega)\int_1^\infty\int_{-1}^1[(Z_1+Z_2)\xi + (Z_1-Z_2)\eta]G_\nu(\xi)G_{\nu'}(\xi)F_\nu F_{\nu'}(\eta)d\xi\, d\eta=\delta_{\nu\nu'}. \tag{3.45}$$

Using same manipulations as for evaluating normalization constants one obtains

$$\frac{1}{2}A_\nu(\omega)A_{\nu'}(\omega)\Bigg\{(Z_1+Z_2)D_{\nu\nu'}^{(0)}\sum_{k=0}^{K_\xi}[2I_{k+m}(\sigma_\nu+\sigma_{\nu'} +1,2\sqrt{2\omega})-I_{k+m}(\sigma_\nu+\sigma_{\nu'},2\sqrt{2\omega})]B_{\nu\nu'}^k+(Z_1 -Z_2)D_{\nu\nu'}^{(1)}\sum_{k=0}^{K_\xi}I_{k+m}(\sigma_\nu+\sigma_{\nu'},2\sqrt{2\omega})B_{\nu\nu'}^k\Bigg\}=\delta_{\nu\nu'}, \tag{3.46}$$

where

$$B_{\nu\nu'}^k=\sum_{s=0}^k g_s^\nu g_{k-s}^{\nu'},\quad D_{\nu\nu'}^{(k)}=\int_{-1}^1\eta^kF_\nu(\eta)F_{\nu'}(\eta)d\eta. \tag{3.47}$$

Since the $F_\nu(\eta)$ are expanded in terms of spherical harmonics the integration over η is easily performed:

$$D_{\nu\nu'}^{(0)}=\sum_{s=m}^{K_\eta}f_s^\nu f_s^{\nu'},$$

$$D_{\nu\nu'}^{(1)}=\sum_{s=m}^{K_\eta-1}(f_s^\nu f_{s+1}^{\nu'}+f_{s+1}^\nu f_s^{\nu'})\sqrt{\frac{(s+m+1)(s-m+1)}{(2s+1)(2s+3)}},$$

$$D_{\nu\nu'}^{(2)}=\sum_{s=m}^{K_\eta}f_s^\nu f_s^{\nu'}\left[\frac{2s^2+2s-1+2m^2}{(2s+3)(2s-1)}\right] +\sum_{s=m}^{K_\eta-2}(f_s^\nu f_{s+2}^{\nu'}+f_{s+2}^\nu f_s^{\nu'}) \times\sqrt{\frac{(s+m+1)(s-m+1)(s+m+2)(s-m+2)}{(2s+1)(2s+5)(2s+3)^2}}. \tag{3.48}$$

5. Matrix elements

Now we consider the matrix elements $M_{\nu\nu'}(\omega)$. After integration over ϕ it becomes

$$M_{\nu\nu'}(\omega)=\frac{1}{8}A_\nu(\omega)A_{\nu'}(\omega)\int_1^\infty\int_{-1}^1(\xi^2-\eta^2) \times G_\nu(\xi)G_{\nu'}(\xi)F_\nu(\eta)F_{\nu'}(\eta)d\xi\, d\eta. \tag{3.49}$$

Using the same arguments as when calculating the normalization constants we obtain

$$M_{\nu\nu'}(\omega)=\frac{1}{4}A_\nu(\omega)A_{\nu'}(\omega)\Bigg[(D_{\nu\nu'}^{(0)}-D_{\nu\nu'}^{(2)})\sum_{k=0}^{K_\xi}I_{k+m}(\sigma_\nu +\sigma_{\nu'},2\sqrt{2\omega})+4D_{\nu\nu'}^{(0)}\sum_{k=0}^{K_\xi}I_{k+m+1}(\sigma_\nu+\sigma_{\nu'} +2,2\sqrt{2\omega})B_{\nu\nu'}^k\Bigg]. \tag{3.50}$$

IV. RESULTS AND DISCUSSION

According to the general Sturm-Liouville theory, when $\omega<0$, the Sturmian eigenvalues and eigenfunctions are real and the number of notes of quasiradial wave functions (n_ξ) and quasiangular wave functions (n_η) are conserved when the parameter ω varies. In classification of Sturmian functions we will use united-atom spherical quantum numbers $\nu=(n,l,m)$ ($1s\sigma$, $2s\sigma$, $2p\sigma$, $2p\pi$, ...). These numbers are related to n_ξ and n_η by

$$n=n_\xi+n_\eta+m+1,\quad l=n_\eta+m \tag{4.1}$$

and are determined by $\rho_\nu(\omega)$ and $\lambda_\nu(\omega)$ in the limit $\omega\to0$,

$$\rho_\nu(\omega)=\frac{\sqrt{-2\omega}n}{Z_1+Z_2}+O(\omega^{3/2}),\quad \lambda_\nu(\omega)=l(l+1)+O(\omega). \tag{4.2}$$

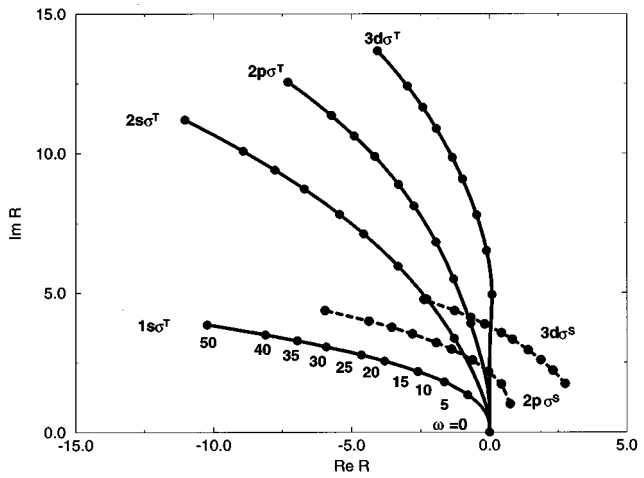

FIG. 1. Trajectories of the Sturmian eigenvalues as a function of ω for $Z_1=Z_2=1$. The dashed curve are the trajectories of the S-type Sturmian functions defined only for $\omega>0$. The solid are the trajectories of the T-type Sturmian functions.

Our computations reveal two different types of Sturmian functions at $\omega>0$, which we call T- and S-type Sturmian functions. Together, these two types of Sturmian functions form a complete set, but they otherwise have rather different properties, which we consider below.

The T-type Sturmian functions are analytic continuations of the negative energy Sturmian functions and therefore exist for all ω. They have the value $\rho_\nu^T(0)=0$ at $\omega=0$ and are similar to the one-Coulomb-center Sturmian functions, especially when $\omega\approx 0$. In the classification of T-type Sturmian functions we will use spherical quantum numbers $\nu=(n,l,m)^T$ $(1s\sigma^T,\ 2s\sigma^T,\ 2p\sigma^T,\ 2p\pi^T,\ \ldots)$ in the limit $\omega\to 0$:

$$\rho_\nu^T(\omega)=\frac{i\sqrt{2\omega}n}{Z_1+Z_2}+O(\omega^{3/2}),\quad \lambda_\nu^T(\omega)=l(l+1)+O(\omega). \tag{4.3}$$

Figure 1 shows trajectories of Sturmian eigenvalues as functions of ω for $Z_1=Z_2=1$.

The quasiradial equation (3.6) is only slightly different from the one-Coulomb-center radial equation at small $q=\xi-1$. But this slight difference brings different features to the Sturmian spectrum, namely, S-type Sturmian eigenfunctions. In contrast to the T-type Sturmian functions, the S-type Sturmian function are defined only for $\omega>0$ and $\rho_\nu^S(0)\neq 0$. In the case $Z_1=Z_2$ the solutions of Eq. (3.7) are generalized Legendre polynomials and $\lambda_\nu^S(\omega)\to l(l+1)$, as $\omega\to 0$, and the value of $\rho_\nu^S(0)$ can be calculated from the semiclassical quantization equation

$$\frac{2}{\pi}[\rho(0)(Z_1+Z_2)+\lambda]^{1/2}\left\{K\left(\frac{\rho(0)(Z_1+Z_2)-\lambda}{\rho(0)(Z_1+Z_2)+\lambda}\right)-E\left(\frac{\rho(0)(Z_1+Z_2)-\lambda}{\rho(0)(Z_1+Z_2)+\lambda}\right)\right\}=\pm\left(\kappa+\frac{m+1}{2}\right), \tag{4.4}$$

where $K(x)$ and $E(x)$ are complete elliptic integrals, $\kappa=0,1,2,\ldots,\kappa_m$, and the κ_m's are determined from the conditions $\mathrm{Re}\rho_\nu^S(0)>0$. A series expansions of the elliptic integrals in Eq. (4.4) gives the following approximate solutions for $\rho_\nu^S(0)$:

$$\rho_\nu^S(0)\approx\frac{(l+1/2)^2}{Z_1+Z_2}\exp\left[\frac{i\pi(2\kappa+m+1)}{2l+1}\right]-\frac{1}{2}. \tag{4.5}$$

From Eq. (4.5) we see that $\kappa_m<\frac{1}{2}(l-m-1/2)$. In the classification of S-type Sturmian functions we will use the quantum numbers l, m, and $n=l+\kappa+1$. Then the set of S-type Sturmian functions is $2p\sigma^S$, $3d\sigma^S$, $3d\pi^S$, $4f\sigma^S$, $4f\pi^S$, $4f\delta^S$, $5f\sigma^S$, $5g\sigma^S$, $5g\pi^S$, $5g\delta^S$, $\ldots$.

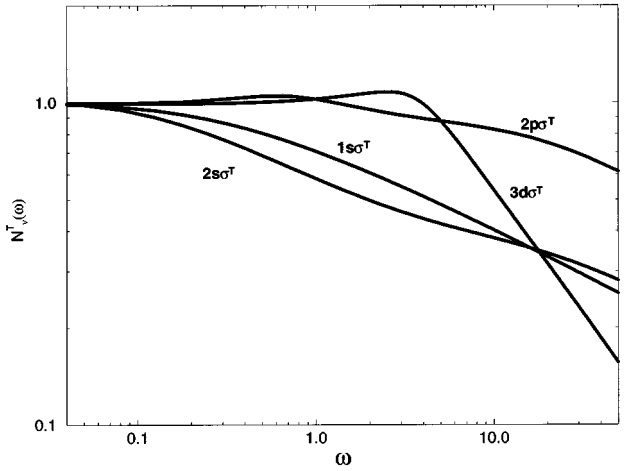

FIG. 2. Results of the numerical calculations of $|N_\nu(\omega)|$ [Eq. (4.8)] for T-type Sturmian functions as a function of ω.

The asymptotic Sturmian eigenvalues $\rho_\nu(\omega)$ for sufficiently large positive ω are just those of uncoupled harmonic oscillators on ξ and η coordinates and for $Z_1=Z_2$ have the form

$$\rho_\nu(\omega)=-\frac{\omega}{2(Z_1+Z_2)}+\frac{1}{Z_1+Z_2}\times\sqrt{\frac{\omega}{2}}[2n'_\eta+1+i\sqrt{2}(2n'_\xi+m+1)]+O(1),$$

$$\lambda_\nu(\omega)=-\frac{\omega}{2}+\sqrt{\frac{\omega}{2}}(2n'_\eta+1)+O(1), \tag{4.6}$$

where $n'_\xi=0,1,\ldots$ and $n'_\eta=0,1,\ldots$ are the quasiradial and quasiangular quantum numbers of harmonic oscillators, respectively, and related to n_ξ and n_η by

$$n'_\xi=n_\xi+\mathrm{Int}\left[\frac{1}{2}\left(l-m-\frac{1}{2}\right)\right],\quad n'_\eta=n_\eta, \tag{4.7}$$

where $\mathrm{Int}[x]$ is the integer part of x.

When $\omega\to 0$ the function $C_\nu^T(\omega)$ associated with T-type Sturmian functions converges to $C_{nl}(\omega)$ associated with united-atom one-Coulomb-center Sturmian function. Figure 2 shows the ratio of C_ν^T [Eq. (3.44)] and C_{nl} [Eq. (D4)]

$$N_\nu^T(p)=\frac{C_\nu^T(\omega)}{C_{nl}(\omega)}, \tag{4.8}$$

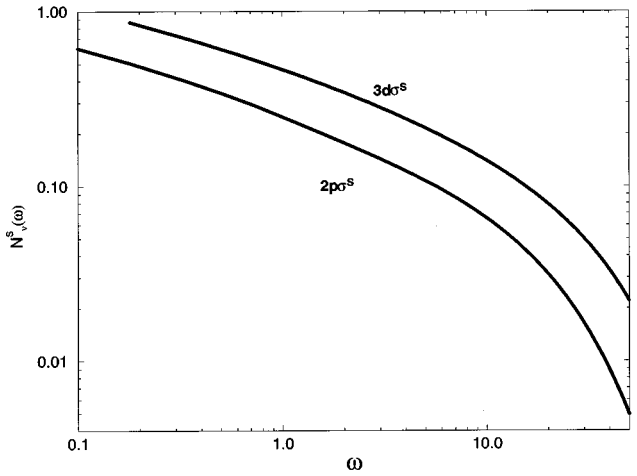

FIG. 3. Results of the numerical calculations of $|N_\nu(\omega)|$ [Eq. (4.10)] for T-type Sturmian functions as a function of ω.

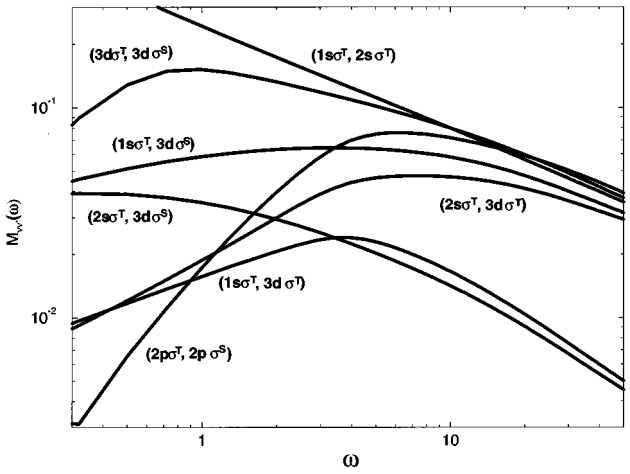

FIG. 4. Coupling matrix elements $|M_{\nu\nu'}(\omega)|$ [Eq. (3.50)] as a function of ω.

for T-type Sturmian functions as a function of ω.

For S-type Sturmian functions the normalization factors $C^S_\nu(\omega)$ diverge as $\omega\to 0$ and have the form

$$C^S_\nu(\omega)=\sqrt{2\pi}\exp\left[\sigma_\nu(\omega)-\sigma_\nu(\omega)\ln\left(\frac{i\sigma_\nu(\omega)}{2\sqrt{2\omega}}\right)\right]+O(\omega^{1/2}),$$

$$\sigma_\nu(\omega)=-i\frac{\rho(\omega)(Z_1+Z_2)}{\sqrt{2\omega}}. \tag{4.9}$$

To present the results of numerical calculations we introduce the regularized normalization factors $C^r_\nu(\omega)$ defined by

$$N^S_\nu(p)=\frac{1}{\sqrt{2\pi}}C^S_\nu(\omega)\exp\left[-\sigma_\nu(\omega)+\sigma_\nu(\omega)\ln\left(\frac{i\sigma_\nu(\omega)}{2\sqrt{2\omega}}\right)\right]. \tag{4.10}$$

The regularized normalization factors $N^S_\nu(p)$ as functions of ω are shown in Fig. 3. At large positive ω the normalization factors $C_\nu(\omega)$ asymptotically behave as

$$C_\nu(\omega)\sim\omega^{n_\xi+(m+1)/2}. \tag{4.11}$$

The coupling matrix elements between $\nu=(nlm)$ and $\nu'=(n+1,lm)$ have pole singularities at $\omega=0$. All other coupling matrix elements are small. Figure 4 shows the coupling matrix elements $|M_{\nu\nu'}(\omega)|$ [Eq. (3.50)].

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APPENDIX A: COMPLETENESS OF OUTGOING STURMIANS

Let us consider the short-range potentials $V(q)$ and $K_2(q)$. If b is finite and $b\gg 1$ we introduce $q_0<b$ and set $V(q)=0$ for $q>q_0$. Then, according to the Sturm-Liouville theorem, both sets $S^{(c)}_\nu(\omega)$ and $S^{(s)}_\nu(\omega)$ defined by the boundary condition (2.3),

$$\left.\frac{\partial S^{(c)}_\nu(\omega;q)}{\partial q}\right|_{q=b}+pS^{(c)}_\nu(\omega;b)=0 \tag{A1}$$

and

$$\left.\frac{\partial S^{(s)}_\nu(\omega;q)}{\partial q}\right|_{q=b}-pS^{(s)}_\nu(\omega;b)=0 \tag{A2}$$

are complete in the space L_V on the interval $a\leqslant q\leqslant b$. The linear combination of the two sets $S^{\rm out}_\nu=S^{(c)}_\nu+iS^{(s)}_\nu$ also forms a complete set and the boundary condition at $q=b$ becomes the outgoing-wave boundary condition (2.9)

$$\left.\frac{\partial S^{\rm out}_\nu(\omega;q)}{\partial q}\right|_{q=b}-ipS^{\rm out}_\nu(\omega;b)=0. \tag{A3}$$

The limit $q_0\to b$ exists since b is finite. Then the matrix elements

$$\langle S_\nu(\omega)(\omega)|V|S_{\nu'}(\omega)\rangle\lim_{b\to\infty}\int_a^b S_\nu(\omega;q)V(q)S_{\nu'}(\omega;q)dq$$
$$=\delta_{\nu\nu'}<\infty \tag{A4}$$

are finite and the outgoing Sturmian functions form a complete set in the space L_V. In this case incoming waves can be expanded in terms of outgoing Sturmian functions.

As an example consider the Sturm-Liouville problem (2.1) with $V(q)=\exp(-2q)$, $K_1(q)=1$, and $K_2(q)=0$ in interval $0\leqslant q<\infty$ with the outgoing-wave boundary condition (2.9). Then Sturmian functions have the form

$$S_\nu(p;q)=J_{ip}(\sqrt{\rho_\nu}e^{-q}), \tag{A5}$$

where $J_{ip}(x)$ is a Bessel function. The eigenvalues ρ_ν are determined by the equation

$$J_{ip}(\sqrt{\rho_\nu})=0. \tag{A6}$$

The Sturmian expansion of the incoming Sturmian function $J_{-ip}(\sqrt{\rho_\nu}\exp(-q))$ in terms of the outgoing Sturmian functions has the form

$$J_{-ip}(\sqrt{\rho_\nu^*}e^{-q})=\sum_{\nu'} A_{\nu\nu'}(p)J_{ip}(\sqrt{\rho_{\nu'}}\,e^{-q}), \quad \text{(A7)}$$

$$A_{\nu\nu'}(p)=\int_0^\infty S_\nu(-p;q)V(q)S_{\nu'}(p;q)dq$$

$$=\int_0^1 tJ_{-ip}(\sqrt{\rho_\nu^*}t)J_{ip}(\sqrt{\rho_{\nu'}}t)dt$$

$$=\frac{2}{|\Gamma(1+ip)|^2}\frac{1}{\rho_\nu^*-\rho_{\nu'}}. \quad \text{(A8)}$$

For large ν', $A_{\nu\nu'}(p)\propto 1/\nu'$ and the summation in Eq. (A7) converges, but not absolutely.

If $V(q)$ vanishes at infinity as $1/q$, the set of outgoing Sturmian functions is complete in the space L_V^{out} of all piecewise continuous functions $f(q)$ on L_V with asymptotic behavior $f\propto q^\alpha\exp(ipq)$ at $q\to\infty$, and $p\geqslant 0$. For this reason it is appropriate to use outgoing- (incoming-) wave Sturmian functions to expand outgoing (incoming) waves even for short-range potentials. Both sets are essential when $V\to 1/q$ as for Coulomb potential.

APPENDIX B: HELLMAN-FEYNMANN PROPERTIES

The Hellman-Feynmann properties of Eqs. (3.6) and (3.7) are

$$\int_1^\infty (Z_1+Z_2)\xi F^2(\xi)d\xi=\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\rho}\int_1^\infty F^2(\xi)d\xi,$$

$$\int_{-1}^1 (Z_1-Z_2)\,\eta G^2(\eta)d\eta=-\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\rho}\int_{-1}^1 G^2(\eta)d\eta,$$

$$\int_1^\infty (\xi^2-1)F^2(\xi)d\xi=2\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\omega}\int_1^\infty F^2(\xi)d\xi,$$

$$\int_{-1}^1 (1-\eta^2)G^2(\eta)d\eta=-2\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\omega}\int_{-1}^1 G^2(\eta)d\eta, \quad \text{(B1)}$$

where the derivatives $\partial\lambda_\xi/\partial\rho$, $\partial\lambda_\eta/\partial\rho$, $\partial\lambda_\xi/\partial\omega$, and $\partial\lambda_\eta/\partial\omega$ are given by

$$\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\rho}=-\frac{\dfrac{\partial D_\xi(\lambda,\rho,\omega)}{\partial\rho}}{\dfrac{\partial D_\xi(\lambda,\rho,\omega)}{\partial\lambda}},$$

$$\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\rho}=-\frac{\dfrac{\partial D_\eta(\lambda,\rho,\omega)}{\partial\rho}}{\dfrac{\partial D_\eta(\lambda,\rho,\omega)}{\partial\lambda}} \quad \text{(B2)}$$

and

$$\frac{\partial\lambda_\xi(\rho,\omega)}{\partial\omega}=-\frac{\dfrac{\partial D_\xi(\lambda,\rho,\omega)}{\partial\omega}}{\dfrac{\partial D_\xi(\lambda,\rho,\omega)}{\partial\lambda}},$$

$$\frac{\partial\lambda_\eta(\rho,\omega)}{\partial\omega}=-\frac{\dfrac{\partial D_\eta(\lambda,\rho,\omega)}{\partial\omega}}{\dfrac{\partial D_\eta(\lambda,\rho,\omega)}{\partial\lambda}}. \quad \text{(B3)}$$

APPENDIX C: THE CALCULATION OF $I_0(a,x)$

The function $I_0(a,x)$ is determined by

$$I_0(a,x)=e^{ix}(-ix)^{-a}\Gamma(a,ix). \quad \text{(C1)}$$

The recurrence formula

$$I_0(a-1,x)=a^{-1}[ixI_0(a,x)-1] \quad \text{(C2)}$$

enables us to reduce a. To calculate $I_0(a,x)$ we use the infinite continued fraction representation of the incomplete Γ function

$$I_0(a,x)=\frac{1}{ix+}\,\frac{1-a}{1+}\,\frac{1}{ix+}\,\frac{2-a}{1+}\,\frac{2}{ix+}\;\cdots. \quad \text{(C3)}$$

If $x>0$ the infinite continued fraction is convergent.

APPENDIX D: ONE-COULOMB-CENTER STURMIANS

Outgoing-wave Coulomb Sturmian functions are obtained by solving Eq. (2.16) with $V(q)=-Z/q$. The general solution is well known to be a linear combination of Coulomb functions F_l and G_l [6]. Imposing outgoing-wave boundary conditions selects the combination F_l+iG_l and the requirement that the solution is regular at the origin gives the Sturmian eigenvalues

$$\rho_n(\omega)=i\frac{np}{Z}, \quad p=\sqrt{2\omega}, \quad n=1,2,\ldots . \quad \text{(D1)}$$

The explicit form of the corresponding outgoing-wave Coulomb Sturmian functions normalized according to Eq. (2.18) are [3]

$$S_{nl}(\omega;\mathbf{q})=\frac{2^{l+1}ip}{(2l+1)!}\sqrt{\frac{(n+l)!}{(n-l-1)!Z}}(pq)^l e^{ipq}{}_1F_1(l+1$$

$$-n,2l+2;-2ipq)Y_{lm}(\hat{\mathbf{q}})$$

$$=\sqrt{\frac{(n-l-1)!}{(n+l)!Z}}2^{l+1}ip(pq)^l e^{ipq}L_{n-l-1}^{(2l+1)}$$

$$\times(-2ipq)Y_{lm}(\hat{\mathbf{q}}), \quad \text{(D2)}$$

where $Y_{lm}(\hat{\mathbf{q}})$ are the spherical harmonics and $L_{n-l-1}^{(2l+1)}$ are generalized Laguerre polynomials [6].

The asymptotic form of $S_{nl}(\omega;\mathbf{q})$ at large q is

$$S_{nl}(\omega;\mathbf{q})\sim C_{nl}(\omega;\hat{\mathbf{q}})q^{n-1}e^{ipq}, \quad \text{(D3)}$$

where

$$C_{nl}(\omega;\hat{\mathbf{q}})=\frac{(-1)^{l+1}}{\sqrt{(n+l)!(n-l-1)!Z}}(-2pi)^n Y_{nl}(\hat{\mathbf{q}}). \tag{D4}$$

The outgoing-wave Coulomb Sturmian functions are polynomials (Laguerre polynomials) in q. The low-order functions $(Z=1)$ are

$$S_{10}(\omega;\mathbf{q})=2ipe^{ipq}Y_{00}(\hat{\mathbf{q}}),$$

$$S_{20}(\omega;\mathbf{q})=\sqrt{8}ipe^{ipq}(1+ipq)Y_{00}(\hat{\mathbf{q}}),$$

$$S_{21}(\omega;\mathbf{q})=2\sqrt{\frac{2}{3}}ip^2qe^{ipq}Y_{10}(\hat{\mathbf{q}}). \tag{D5}$$

The matrix elements of the Sturmian functions are readily evaluated using recurrence relations for Laguerre polynomials. For all n the matrix elements $M_{nn}(p)$ and $M_{nn\pm1}(p)$, Eq. (2.13) have poles at $p=0$,

$$M_{nn}(p)=-\frac{n}{Zp},$$

$$M_{nn+1}(p)=\frac{\sqrt{n+l+1}}{2Zp},$$

$$M_{nn-1}(p)=\frac{\sqrt{n+l}}{2Zp},$$

$$M_{nn'}(p)=0 \quad \text{otherwise.} \tag{D6}$$

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