Theory of ionization in ion-atom collisions: Spectra of ejected electrons

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A Galilean invariant theory of atomic collisions is constructed for straight-line trajectories of nuclei with arbitrary impact parameters. The theory is based on Sturmian expansions in Fourier space, and provides an exact description of excitation and ionization processes for a wide range of collision velocities. Advantages of Sturmian sets over conventional eigenstates are emphasized. Detailed spectra of electrons ejected in head-on ion-atom collisions are calculated. [S1050-2947(97)04210-8]

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I. INTRODUCTION

Ionization in ion-atom collisions is of continued theoretical interest, especially at low collision energies. Because the relative velocity of nuclei is less than the mean electron velocity in the initial state, physical processes are often described in terms of adiabatic eigenstates and the corresponding instantaneous energy values. The approximate separation of nuclear and electronic motion is referred to here as the Born-Oppenheimer approximation. This approach has had considerable qualitative success, but well-formulated, completely *ab initio* computations in this representation have proved problematical. For example, it is known that the adiabatic eigenstates must be supplemented by translational factors to achieve a Galilean invariant theory. Even then, ionization cannot be properly described owing to the failure of the Born-Oppenheimer approximation for electrons moving slowly relative to the positively charged nuclei in the final state.

The failure of the Born-Oppenheimer separation of variables ultimately derives from the lack of Galilean covariance of Schrödinger plane waves $\phi_{\mathbf{k}}(t,\mathbf{r})$. Plane waves are not invariant in form under the transformation $\mathbf{r}'=\mathbf{r}+\mathbf{v}t$, $\mathbf{k}'=\mathbf{k}+\mathbf{v}$, $t'=t$, rather, the functions $\phi_{\mathbf{k}}(t,\mathbf{r})$ and $\phi_{\mathbf{k}'}(t',\mathbf{r}')$ differ by phase factors. These same phase factors, known as the Bates-McCarroll [1] translations factors, are easily included in atomic basis expansions to obtain a Galilean invariant theory, but are foreign to the Born-Oppenheimer separation of variables. Several workers have introduced *ad hoc* translation factors [2–4] better adapted to the Born-Oppenheimer separation of variables. Such factors prove superior to the plane-wave factors for transitions involving bound states, although they meet with difficulties for breakup channels.

An alternative approach was used by Solov'ev and Vinitsky [5]. They constructed a satisfactory theory by finding a coordinate frame in which the Born-Oppenheimer separation of variables emerges naturally. In such a coordinate frame the positions of the target-electron and projectile electron potentials do not change with time. Transformations to this frame are accomplished by first transforming to a frame that rotates with the internuclear axis. Because transformations to rotating frames are standard in the theory of ion-atom collisions, this aspect of Solov'ev and Vinitsky's representation is not reviewed here.

Solov'ev and Vinitsky also introduced a coordinate system with a length scale that changes with time, such that the distance between the target and projectile is fixed in this new system of scaled coordinates. The transformation to a frame with a length scale that changes with time is nonlinear. In addition, a new time variable is introduced to write the transformed time-dependent Schrödinger equation in its familiar form. Solov'ev and Vinitsky's transformation is reviewed in Sec. III.

Although the scaled coordinates were introduced to insure a Galilean invariant theory, they played no essential role in the theory of Ref. [5]. This role becomes apparent when we consider Born-Oppenheimer wave functions for continuum states. As $r\to 0$ the electron wave function approaches that of an electron in the potential $-Z_{\mathrm{ua}}/r$, where Z_{ua} is the united-atom charge and r is the electron coordinate relative to the center of charge. It follows that the normalization of the continuum electron states of energy $E_{\mathbf{k}}=k^2/2$ includes the factor $N=\exp[\pi\nu/2]\Gamma(1+i\nu)$, where $\nu=Z_{\mathrm{ua}}/k$ is Sommerfeld's parameter. The square of the normalization constant as $k\to 0$ appears as a factor in the Galilean invariant cross section $d^3\sigma/dk^3$, and is singular in the limit as $k\to 0$. This singularity at $k=0$ is known to be incorrect, rather the Galilean invariant cross section has two singularities at $|\mathbf{k}-\mathbf{v}_P|$ and $|\mathbf{k}-\mathbf{v}_T|$, where $\mathbf{v}_P$ and $\mathbf{v}_T$ are the final-state velocities of the projectile and target, respectively. The two singularities correspond physically to the well-known continuum capture and electron loss cusps. It follows that Born-Oppenheimer adiabatic basis functions cannot give the low-energy electron spectra correctly no matter what sort of *ad hoc* translational factors are employed. This remark applies to all representations including Solov'ev and Vinitsky's representation used here and traces the difficulty to the adiabatic basis set. For that reason we consider an alternative basis, namely, the H_2^+ Sturmian basis discussed in an earlier paper [6] and reviewed in Appendix C.

Sturmian bases are defined such that the coefficient $\rho_n(\omega)$ of the scaled potential $V(\mathbf{q})$ is used as an eigenvalue for fixed values of the energy parameter $\omega=ER^2$. The corre-

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sponding Sturmian eigenfunctions are denoted by $S_n(\omega;\mathbf{q})$, and are defined for all values of ω, including positive, negative, and even complex values. In contrast to the adiabatic functions, the Sturmian functions do not depend, even parametrically, upon the internuclear distance R. When this basis set is used, the R and t dependences emerge from the solution of the dynamical equations.

The Sturmian functions depend parametrically upon ω, which is a frequency conjugate to the time variable τ. For that reason we transform the dynamical equations to the frequency domain via a Fourier transform. The transformation to the frequency domain is discussed in Sec. IV.

The emergence of Sturmian functions in the time domain can be understood by noting that two-center Coulomb potentials scale as $V(\mathbf{q})/R(t)$, where the scaled coordinate $\mathbf{q}=\mathbf{r}/R(t)$ is dimensionless. In the frequency domain R becomes a frequency-dependent operator. It is then natural to seek a representation where the coefficient of this operator is diagonal and proportional to the unit matrix. The Sturmian basis is uniquely determined by this requirement.

The ''advanced adiabatic theory'' of Solov'ev [7] employs a philosophy very similar to the present work, but differs in two critical ways from the development presented here. The ''advanced adiabatic theory'' does not employ the scaling transformation, thus it is based upon a Galilean not-invariant bases. To some extent this is a formal matter, but it does affect the mathematical form that the important innovation of Ref. [7] takes. This innovation was to define a function $R(E)$ inverse to the adiabatic energy eigenvalue $E(R)$ and to employ a set of associated basis states $\varphi(R(E),\mathbf{r})$. It can be shown that this set is not complete in the usual sense. In contrast, the present theory uses the scaling transformation to effect a Galilean invariant representation [5]. This transformation introduces the product $E(R)R^2$ in place of $E(R)$ in the Schrödinger equation, and the potential has the scaled form $RV(\mathbf{q})$. The coefficient of $V(\mathbf{q})$ in the Schrödinger equation is used as an eigenvalue. The functions, thus defined, are a complete set of Sturmian functions and are well suited to exact calculations. The Sturmian eigenvalues $\rho_n(\omega)$ are seen to be roots of the equation $E(\rho)\rho^2=\omega=\text{const}$, whereas the quantity $R(E)$ of Ref. [7] is a root of the equation $E(R)=E$. The presence of the ρ^2 factor gives a very different spectrum of eigenvalues and eigenfunctions for the Sturmian functions than for the quantity $R(E)$ and the associated functions $\varphi(R(E),\mathbf{r})$ of the advanced adiabatic theory.

Recently, to calculate the spectra of electrons ejected in head-on collisions (straight-line trajectories of nuclei with zero impact parameter) with a very broad range of relative velocities, positive energy Sturmian functions for the two-center Coulomb potential have been employed [8]. In this manuscript we consider the general Sturmian theory of atomic collisions based on positive energy Sturmian functions for straight line trajectories of nuclei with arbitrary impact parameter. (Atomic units are used throughout.)

II. TIME-DEPENDENT SCHRÖDINGER EQUATION

The time-dependent Schrödinger equation used in the theory of ion-atom collisions has the form

$$\left[i\frac{\partial}{\partial t} - H(\mathbf{R},\mathbf{r}) \right] \psi(t,\mathbf{r}) = 0, \tag{2.1}$$

where $\mathbf{R}=\mathbf{R}_A-\mathbf{R}_B$ and $\mathbf{R}_A, \mathbf{R}_B, =\mathbf{r}$ are the vectors determining the positions of two nuclei A and B, and the electron with respect to the center of mass. We assume here that nuclear motion can be treated classically, and the time-dependent internuclear distance $R(t)=|\mathbf{R}|$ is defined by the trajectory of relative motion of the nuclei. Usually, initial conditions are imposed at $t\to-\infty$ for $\psi^-(t,\mathbf{r})$ and $t\to\infty$ for $\psi^+(t,\mathbf{r})$. The equality $\psi^+(t,\mathbf{r})=\psi^-(-t,-\mathbf{r})^*$ allows us to define the initial conditions for both initial and final states at $t\to-\infty$, and describe collisional processes on the semi-infinite time axis $-\infty<t\leqslant 0$. Transition amplitudes to the continuum are given by the matrix elements [9]

$$T_{\mathbf{k},i}=\langle \psi_{\mathbf{k}}^+(t)|\psi_i^-(t)\rangle \equiv \int [\psi_{\mathbf{k}}^+(t,\mathbf{r})]^* \psi_i^-(t,\mathbf{r}) d^3\mathbf{r}. \tag{2.2}$$

The initial conditions associated with an electron that is bound in an atomic state $\phi_i(\mathbf{r}_a)$ of the particle A with an eigenenergy E_i are

$$\psi_i^-(t,\mathbf{r}) \underset{t\to-\infty}{\sim} \phi_i(\mathbf{r}_a) e^{-iE_it} e^{i\mathbf{v}_a\cdot\mathbf{r}_a + iv_a^2 t/2}, \tag{2.3}$$

where $\mathbf{r}_a=|\mathbf{r}-\mathbf{R}_A|$, $\mathbf{v}_a=M_B\mathbf{v}/(M_B+M_A)$, M_A, and M_B are the masses of nuclei A and B, and $\mathbf{v}$ is the relative collision velocity. In terms of adiabatic eigenstates $\Phi_\nu(R(t);\mathbf{r})$ and eigenvalues $E_\nu(t)$ the initial conditions become

$$\psi_i^-(t,\mathbf{r}) \underset{t\to-\infty}{\sim} \sum_\nu a_\nu^i \Phi_\nu(R(t);\mathbf{r}) e^{-i\int^t E_\nu(t)dt} e^{i\gamma_{\text{trnsl}}(\mathbf{r},t,\mathbf{v})},$$

$$a_\nu^i = \lim_{R\to\infty} \langle \Phi_\nu(R)|\phi_i\rangle, \tag{2.4}$$

where $E_\nu(t)\to E_i$ as $t\to-\infty$, and $\gamma_{\text{trnsl}}(\mathbf{r},t,\mathbf{v})$ is a translation factor that insures the Galilean invariance of the function $\psi_i^-(t,\mathbf{r})$:

$$\gamma_{\text{trnsl}}(\mathbf{r},t,\mathbf{v}) \underset{t\to-\infty}{\sim} \mathbf{v}_a\cdot\mathbf{r}_a + v_a^2 t/2. \tag{2.5}$$

The incoming part of the final ionization state with an electron of a wave vector $\mathbf{k}$ is represented explicitly as

$$\psi_{\mathbf{k}}^-(t,\mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{r}\cdot\mathbf{k} - ik^2 t/2)\Theta(t-T_0) + \psi_{\mathbf{k}}^{\text{scat}}(t,\mathbf{r}), \tag{2.6}$$

with the initial condition $\psi_{\mathbf{k}}^{\text{scat}}(t,\mathbf{r})=0$ as $t\leqslant T_0$. Then the functions $\psi_i^-(t,\mathbf{r})$ and $\psi_{\mathbf{k}}^-(t,\mathbf{r})$ are orthogonal as $T_0\to-\infty$:

$$\langle \psi_{\mathbf{k}}^-(t)|\psi_i^-(t)\rangle \to 0 \quad \text{as} \quad T_0\to-\infty. \tag{2.7}$$

It should be emphasized here that the $\{t,\mathbf{r}\}$ space is not particularly convenient for the solution of dynamic problems in atomic collisions, because the adiabatic basis states $\{\Phi_\nu(R,\mathbf{r})\}$ do not satisfy the initial conditions (2.3) (not Galilean invariant). Although this basis describes very well the electron motion in the relevant potentials, it is difficult to

satisfy the initial conditions (2.3) without proper translation factors. In particular, many matrix elements of the nonadiabatic coupling remain finite even at infinitely large internuclear distances [10]

$$\left\langle \Phi_{\nu'}(R)\left|\frac{\partial}{\partial R}\right|\Phi_{\nu}(R)\right\rangle \sim \text{const} \quad \text{as} \quad R\to\infty. \tag{2.8}$$

This circumstance led to the development of a host of translation factor theories [10]. In the Sec. III we present an analytic approach to this problem that is the most suitable for use with the Sturmian representation.

III. SCALED SPACE

In order to take into account explicitly the Galilean properties of the molecular basis sets discussed above, Solov'ev and Vinitsky [5] proposed the following scaled coordinates, in a rotating frame where the z axis points along $\mathbf{R}(t)$,

$$\mathbf{q}=\mathbf{r}/R(t), \tag{3.1}$$

$$\tau=\int_{-\infty}^{t}\frac{dt'}{R^2(t')}, \tag{3.2}$$

and a function transformation

$$\varphi^{-}(\tau,\mathbf{q})=\widetilde{R}^{3/2}(\tau)\exp\left[-i\,\frac{d\widetilde{R}(\tau)/d\tau}{2\widetilde{R}(\tau)}q^2\right]\psi^{-}[t(\tau),\widetilde{R}(\tau)\mathbf{q}], \tag{3.3}$$

where $\widetilde{R}^2(\tau)=dt/d\tau$.

It is possible to show that, when $t\to-\infty$, the exponential in Eq. (3.3) goes to the correct Galilean factor. Thus the translational part of the initial conditions Eq. (2.4) is satisfied automatically by the Solov'ev-Vinitsky transformation, i.e.,

$$\exp\left[-i\,\frac{d\widetilde{R}(\tau)/d\tau}{2\widetilde{R}(\tau)}q^2\right]=\exp(-i\,\gamma_{\text{trnsl}}(\mathbf{r},t,\mathbf{v})). \tag{3.4}$$

The function $\varphi(\tau,\mathbf{q})$ satisfies the following time-dependent Schrödinger equation in the $\{\tau,\mathbf{q}\}$ space:

$$\left[i\frac{\partial}{\partial\tau}-H_0(\mathbf{q})-\widetilde{R}(\tau)V(\mathbf{q})-\tfrac{1}{2}\Omega^2(\tau)q^2-\Omega(\tau)\hat{L}_y\right]\varphi(\tau,\mathbf{q})=0, \tag{3.5}$$

where

$$V(\mathbf{q})=\left(-\frac{Z_1}{|\mathbf{q}-\hat{\mathbf{R}}/2|}-\frac{Z_2}{|\mathbf{q}+\hat{\mathbf{R}}/2|}\right),\quad H_0(\mathbf{q})=-\tfrac{1}{2}\nabla_{\mathbf{q}}^2, \tag{3.6}$$

$$\Omega^2(\tau)=\frac{1}{\widetilde{R}(\tau)}\frac{d^2\widetilde{R}(\tau)}{d\tau^2}-2\left(\frac{1}{\widetilde{R}(\tau)}\frac{d\widetilde{R}(\tau)}{d\tau}\right)^2. \tag{3.7}$$

The term with the angular momentum operator $\hat{L}_y$ in Eq. (3.5) occurs because a reference frame that rotates with the frequency $\Omega(\tau)$ is employed. This rotation is essential to obtain proper translational properties of the solution [11]. In this paper we will consider straightline trajectories of nuclei with impact parameter b and relative velocity v, where the oscillator frequency $\Omega_s(\tau)=vb$ is a constant. The function $\widetilde{R}(\tau)$ in this case is

$$\widetilde{R}(\tau)=-\frac{b}{\sin vb\tau}. \tag{3.8}$$

The initial conditions for bound states (2.4) now become

$$\varphi_i^{-}(\tau,\mathbf{q})\underset{\tau\to0}{\sim}\widetilde{R}^{3/2}(\tau)\sum_{\nu}a_{\nu}\Phi_{\nu}(\widetilde{R}(\tau),\mathbf{q})e^{-i\int_0^{\tau}E_{\nu}(\tau)\widetilde{R}^2(\tau)d\tau}. \tag{3.9}$$

Notice that there is no translation factor, and that functions $\varphi_i(\tau,\mathbf{q})$ are invariant under Galilean transformations.

For the final ionization state it can be shown [12] that the plane-wave part of $\psi_{\mathbf{k}}(t,\mathbf{r})$ is transformed, according to Eq. (3.3), into the propagator of electron motion in the oscillator potential with rotation $K_{\text{osc}}(\mathbf{q},\tau;\mathbf{q}_0,0)$, and the wave function that corresponds to the final ionization state is given by

$$\varphi_{\mathbf{k}}^{-}(\tau,\mathbf{q})=(-iv)^{-3/2}K_{\text{osc}}\left(\mathbf{q},\tau;\frac{\mathbf{k}}{v},0\right)+\varphi_{\mathbf{k}}^{\text{scat}}(\tau,\mathbf{q}), \tag{3.10}$$

with the initial condition $\varphi_{\mathbf{k}}^{\text{scat}}(\tau,\mathbf{q})\to0$ as $\tau\to0$. Using Eqs. (2.2) and (3.3), one easily finds transition amplitudes to the continuum,

$$T_{\mathbf{k},i}=\langle\varphi_{\mathbf{k}}^{+}(\tau)|\varphi_i^{-}(\tau)\rangle. \tag{3.11}$$

In this paper we will also consider a particular case of head-on collisions with zero impact parameter and no interaction between the colliding nuclei. The main simplification thus obtained is that the frequency $\Omega(\tau)$ in Eq. (3.5) is equal to zero, and we can avoid complications connected with the oscillator and rotational terms in Eq. (3.5). It is important to note that in this case the Hamiltonian in Eq. (3.5) depends on τ only through the factor $\widetilde{R}(\tau)$ multiplying the potential $V(\mathbf{q})$.

For zero impact parameter one has

$$\widetilde{R}(\tau)=-\frac{1}{v\tau},\quad -\infty<\tau\leqslant0. \tag{3.12}$$

In this case the incoming plane-wave part of the final ionization state $\psi_{\mathbf{k}}(t,\mathbf{r})$ is transformed, according to Eqs. (3.3) and (3.12), into a Gaussian wave packet, with K_{osc} in Eq. (3.10) replaced by the free-particle propagator K_{free} given by

$$K_{\text{free}}(\mathbf{q},\tau;\mathbf{q}_0,0)=(2\pi i\tau)^{-3/2}\exp\left[\frac{i}{2\tau}(\mathbf{q}-\mathbf{q}_0)^2\right]. \tag{3.13}$$

Note that $K_{\text{free}}(\mathbf{q},\tau;\mathbf{k}/v,0)$ of Eq. (3.13) is covariant (invariant in form) under the Galilean transformation $\mathbf{r}'=\mathbf{r}+\mathbf{v}t$, $\mathbf{k}'=\mathbf{k}+\mathbf{v}$. This covariance of the free-particle solutions suggest that Solov'ev's representation has a more fundamental basis that do *ad hoc* translational factors. Manifest covariance is most important for ionization states.

In the representation described in this section the wave functions $\varphi_i(\tau,\mathbf{q})$ and $\varphi_{\mathbf{k}}(\tau,\mathbf{q})$ are Galilean covariant. In standard theories [13,14], $\psi(\tau,\mathbf{q})$ is expanded in scaled adiabatic (fixed-nucleus) basis states, i.e., eigenstates of H_0+RV. These states cannot represent ionization spectra correctly, and capture-to-continuum cusps are always missing in such calculations. Another problem of scaled adiabatic bases is that *all* matrix elements of the nonadiabatic coupling become infinite at $R=0$. This means that a large number of basis functions must be used to obtain a good representation of ψ. There is also a common problem for all adiabatic representations, namely, the system starts out in one of the lowest adiabatic states, and if it is to evolve to a state where the electron is free, it must cross an infinite number of bound levels. Just how to represent this infinite number of crossings without explicitly putting in all of the basis states is a severe problem for standard basis set expansions. This problem will be addressed by using a sufficiently different set of basis states.

The Solov'ev-Vinitsky transformation introduces an essential singularity at $\tau=0$ into all functions in $\{\tau,\mathbf{q}\}$ space [see, for example, Eq. (3.13)]. As we will see in Sec. IV, the essential singularities disappear when we perform a dynamical separation of variables.

IV. DYNAMICAL SEPARATION OF VARIABLES

A. General formulation

We have seen that adiabatic bases cannot describe ionization, thus we introduce a closely related, but alternative set, the H_2^+-like Sturmian bases [6]. These functions, although formally identical to the adiabatic bases at specific values of the parameter R, do describe ionization channels. The Sturmian functions depend parametrically upon the frequency ω conjugate to the time variable τ. In order to use the Sturmian bases, we write the wave functions as Fourier transforms

$$\varphi^{\pm}(\tau,\mathbf{q})=\frac{1}{\sqrt{-2\pi i}}\int_{-\infty}^{\infty}d\omega\,\exp(-i\omega\tau)\chi^{\pm}(\omega,\mathbf{q}), \tag{4.1}$$

and obtain the following equation for $\chi^{\pm}(\omega,\mathbf{q})$ in $\{\omega,\mathbf{q}\}$ space:

$$i\mathcal{O}_{\omega}^{\Omega_s}\left\{\left[H_0(\mathbf{q})-\frac{1}{2}\Omega_s^2q^2-\Omega_s\hat{L}_y-\omega\right]\chi^{\pm}(\omega,\mathbf{q})\right\}=\frac{1}{v}V(\mathbf{q})\chi^{\pm}(\omega,\mathbf{q}), \tag{4.2}$$

where

$$\Omega_s=vb, \tag{4.3}$$

and the operator $\mathcal{O}_x^a$ is defined as

$$\mathcal{O}_x^a\hat{f}(x)=\frac{\hat{f}(x+a)-\hat{f}(x-a)}{2a} \tag{4.4}$$

for an arbitrary operator $\hat{f}(x)$.

To satisfy the physical initial conditions (3.9) on the functions $\varphi^{\pm}(\tau,\mathbf{q})$, the functions $\chi^{\pm}(\omega,\mathbf{q})$ must satisfy certain initial conditions, but we defer this question to Sec. VI after we build a general solution in Sec. V. We assume here that the proper initial conditions are satisfied, and write the transition amplitude according to Eqs. (2.2) and (4.1),

$$T_{\mathbf{k},i}=\frac{i}{2\pi}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\,e^{-i(\omega-\omega')\tau}\langle\chi_{\mathbf{k}}^{+}(\omega')|\chi_i^{-}(\omega)\rangle. \tag{4.5}$$

Notice that continuum functions $\chi_{\mathbf{k}}(\omega,\mathbf{q})$ can be expressed in terms of the Green's functions of the oscillator with rotation [15],

$$\chi_{\mathbf{k}}(\omega,\mathbf{q})=\frac{1}{\sqrt{2\pi}v^{3/2}}G_{\rm osc}(\omega;\mathbf{q},\mathbf{k}/v)+\chi_{\mathbf{k}}^{\rm scat}(\omega,\mathbf{q}). \tag{4.6}$$

It is shown in Appendix A that transition amplitudes are given in term of residues at the poles of certain integrals [see Eq. (A16)]. The situation is more complex in the $b=0$ case mostly because both discrete and continuum spectra are present in the problem (there is only a discrete spectrum in the $b\neq0$ case). In what follows we consider specific features of the $b=0$ case, which are not present when $b\neq0$.

B. Specific features for $b=0$

It can be seen that, when $\Omega_s\to0$,

$$\mathcal{O}_{\omega}^{\Omega_s}\to\frac{\partial}{\partial\omega}, \tag{4.7}$$

and for the zero impact parameter Eq. (4.2) becomes

$$i\frac{\partial}{\partial\omega}\{[H_0(\mathbf{q})-\omega]\chi^{\pm}(\omega,\mathbf{q})\}=\frac{1}{v}V(\mathbf{q})\chi^{\pm}(\omega,\mathbf{q}). \tag{4.8}$$

In the $b=0$ case, one has to distinguish between incoming and outgoing solutions when dealing with the continuum functions. For instance, wave functions $\chi_{\mathbf{k}}^{\rm out}(\omega,\mathbf{q})$ that correspond to the final continuum state in $\{\omega,\mathbf{q}\}$ space now become

$$\chi_{\mathbf{k}}^{-}(\omega,\mathbf{q})=\frac{1}{\sqrt{2\pi}v^{3/2}}G^{\rm out}(\omega;\mathbf{q},\mathbf{k}/v)+\chi_{\mathbf{k}}^{\rm scat}(\omega,\mathbf{q}), \tag{4.9}$$

where $G^{\rm out}$ is the free-particle Green's function defined by Eq. (C22).

Asymptotically the bound-state functions $\chi_i^{-}(\omega,\mathbf{q})$ and continuum functions $\chi_{\mathbf{k}}^{\rm scat}(\omega,\mathbf{q})$ have similar behavior to short-range potential Sturmian functions, even if V is a long-range potential:

$$\chi_i^{-}(\omega,\mathbf{q})\underset{q\to\infty}{\sim}C_i(\omega,\hat{\mathbf{q}})q^{-1}e^{i\sqrt{2\omega}q}, \tag{4.10}$$

$$\chi_{\mathbf{k}}^{\rm scat}(\omega,\mathbf{q})\underset{q\to\infty}{\sim}C_{\mathbf{k}}(\omega,\hat{\mathbf{q}})q^{-1}e^{i\sqrt{2\omega}q}. \tag{4.11}$$

When $t\to0$ the variable τ becomes infinite, and $q=rv\tau$ goes to infinity as well for all $r\neq0$. Therefore we can use the

asymptotic forms of the wave functions $\chi_i(\omega,\mathbf{q})$ and $\chi_{\mathbf{k}}^{\mathrm{scat}}(\omega,\mathbf{q})$ given by Eqs. (4.10) and (4.11) to evaluate the integral in Eq. (4.1). Since $\tau\to\infty$, the stationary phase method gives asymptotically exact results, and we obtain

$$\psi_i(0,\mathbf{r})=v^{3/2}C_i(\omega_0,\hat{\mathbf{r}}) \tag{4.12}$$

and

$$\psi_{\mathbf{k}}^{\mathrm{scat}}(0,\mathbf{r})=v^{3/2}C_{\mathbf{k}}(\omega_0,\hat{\mathbf{r}}), \tag{4.13}$$

where $\omega_0=v^2r^2/2$ is the point of the stationary phase. It is important to note here that functions

$$\chi^-(\omega,\mathbf{q})=\chi^{\mathrm{out}}(v;\omega,\mathbf{q})$$

and

$$\chi^+(\omega,\mathbf{q})=[\chi^{\mathrm{in}}(-v;\omega,-\mathbf{q})]^* \tag{4.14}$$

automatically have outgoing-wave asymptotics. The indexes ''in'' and ''out'' are meaningful only for $\omega>0$. Both incoming and outgoing Sturmian functions have the same analytic continuation into the $\omega<0$ region. These analytic continuations satisfy bound-state boundary conditions, and, therefore, one should not distinguish between in and out Sturmian functions for $\omega<0$. However, for simplicity of notation, in the following sections we will be using indexes ''in'' and ''out'' even for $\omega<0$. We will use only χ^- functions to find the transition amplitude [see Eq. (4.14)]; therefore we omit this index from now on.

V. STURMIAN EXPANSIONS AND COUPLED EQUATIONS

A. Case $b\neq 0$

We expand the wave functions $\chi_i(\omega,\mathbf{q})$ and $\chi_{\mathbf{k}}^{\mathrm{scat}}(\omega,\mathbf{q})$ in terms of a discrete set of orthonormal Sturmian basis functions:

$$\chi_i(\omega,\mathbf{q})=\sum_\nu S_\nu(\omega;\mathbf{q})B_\nu^i(\omega)$$

and

$$\chi_{\mathbf{k}}^{\mathrm{scat}}(\omega,\mathbf{q})=\sum_\nu S_\nu(\omega;\mathbf{q})B_\nu^{\mathbf{k}}(\omega), \tag{5.1}$$

where the Sturmian functions satisfy the following equation:

$$\left[H_0(\mathbf{q})-\frac{1}{2}\Omega_s^2q^2-\Omega_s\hat{L}_y-\omega\right]S_\nu(\omega;\mathbf{q}) =-\rho_\nu(\omega)V(\mathbf{q})S_\nu(\omega;\mathbf{q}). \tag{5.2}$$

The Sturmian normalization condition is

$$\int \widetilde{S}_\nu(\omega;\mathbf{q})V(\mathbf{q})S_\nu(\omega;\mathbf{q})d^3\mathbf{q}=-1, \tag{5.3}$$

where $\widetilde{S}_\nu(\omega;\mathbf{q})$ is a dual function to $S_\nu(\omega;\mathbf{q})$ obtained by inverting the axis of rotation, i.e., $\Omega_s\to-\Omega_s$. The normalization with dual functions avoids complex conjugation, and allows us to use the analyticity of Sturmian functions in the complex plane of ω.

Our definition of the dual also plays an important role in the invariance of the Sturmian theory under a shift of the coordinate system along the internuclear axis. This invariance was established earlier for the adiabatic representation [11]. The invarience of the Sturmian theory employs similar arguments, and is demonstrated in Appendix B.

Using Eq. (4.2), one easily finds equations for the coefficients $B_\nu^i(\omega)$,

$$\frac{1}{v}B_\nu^i(\omega)+i\sum_{\nu'}\langle\widetilde{S}_\nu(\omega)|-V(\mathbf{q})\mathcal{O}_\omega^{\Omega_s}|B_{\nu'}^i(\omega)\rho_{\nu'}(\omega)S_{\nu'}(\omega)\rangle =0. \tag{5.4}$$

When calculating the inhomogeneous parts in equations for $B_\nu^{\mathbf{k}}(\omega)$, we use the Sturmian expansion of the oscillator Green's function with rotation $G_{\mathrm{osc}}(\omega;\mathbf{q},\mathbf{k}/v)$ in Eq. (4.6),

$$G_{\mathrm{osc}}(\omega;\mathbf{q},\mathbf{k}/v)=\sum_\nu\frac{1}{\rho_\nu(\omega)}\widetilde{S}_\nu(\omega;\mathbf{k}/v)S_\nu(\omega;\mathbf{q}), \tag{5.5}$$

to obtain the following equation:

$$\frac{1}{v}B_\nu^{\mathbf{k}}(\omega)+i\sum_{\nu'}\langle\widetilde{S}_\nu(\omega)|-V(\mathbf{q})\mathcal{O}_\omega^{\Omega_s}|B_{\nu'}^{\mathbf{k}}(\omega)\rho_{\nu'}(\omega)S_{\nu'}(\omega)\rangle =\frac{i}{\sqrt{2\pi v}}\frac{\widetilde{S}_\nu(\omega;\mathbf{k}/v)}{v^2\rho_\nu(\omega)}. \tag{5.6}$$

Using quasiclassical methods [16], one finds that at large negative ω the solutions of the recurrence relation Eqs. (5.4) can be approximated by the formula

$$B_\nu^i(\omega)\underset{\omega\to-\infty}{\sim}\frac{A_\nu^i(-\infty)}{\rho_\nu^{\mathrm{out}}(\omega)}\exp\left[\frac{i}{v}\int_{\omega_0}^{\omega}\frac{d\omega'}{\rho_\nu^{\mathrm{out}}(\omega')}\right]. \tag{5.7}$$

It is convenient to extract the fast variation explicitly, and introduce slowly varying coefficients $A_\nu^i(\omega)$ and $A_\nu^{\mathbf{k}}(\omega)$ by

$$B_\nu^i(\omega)=\frac{A_\nu^i(\omega)}{\rho_\nu(\omega)}\exp\left[\frac{i}{v}\int_{\omega_0}^{\omega}\frac{d\omega'}{\rho_\nu(\omega')}\right]$$

and

$$B_\nu^{\mathbf{k}}(\omega)=\frac{A_\nu^{\mathbf{k}}(\omega)}{\rho_\nu(\omega)}\exp\left[\frac{i}{v}\int_{\omega_0}^{\omega}\frac{d\omega'}{\rho_\nu(\omega')}\right].$$

B. Case $b=0$

In the particular case $b=0$ the equations for the coefficients can be obtained in a similar fashion. Instead of recurrence relations we now have differential equations, and it is necessary to use outgoing Sturmian functions for $\omega>0$. The final equations for $b=0$ are

$$\frac{\partial A^i_\nu(\omega)}{\partial\omega}+\sum_{\nu'\neq\nu}\mathcal{Q}_{\nu\nu'}(\omega)A^i_{\nu'}(\omega)=0 \tag{5.8}$$

and

$$\frac{\partial A^{\mathbf{k}}_\nu(\omega)}{\partial\omega}+\sum_{\nu'\neq\nu}\mathcal{Q}_{\nu\nu'}(\omega)A^{\mathbf{k}}_{\nu'}(\omega)=\mathcal{P}^{\mathbf{k}}_\nu(\omega), \tag{5.9}$$

where

$$\mathcal{Q}_{\nu\nu'}(\omega)=\left\langle S^{\rm out}_\nu(\omega)\left|-V\frac{\partial}{\partial\omega}\right|S^{\rm out}_{\nu'}(\omega)\right\rangle \times\exp\left\{\frac{i}{v}\int_{\omega_0}^{\omega}d\omega'\left[\frac{1}{\rho^{\rm out}_{\nu'}(\omega')}-\frac{1}{\rho^{\rm out}_{\nu}(\omega')}\right]\right\},$$

$$\mathcal{P}^{\mathbf{k}}_\nu(\omega)=\frac{i}{\sqrt{2\pi v}}\exp\left[-\frac{i}{v}\int_{\omega_0}^{\omega}\frac{d\omega'}{\rho^{\rm out}_\nu(\omega')}\right]\frac{S^{\rm out}_\nu(\omega;\mathbf{k}/v)}{v^2\rho^{\rm out}_\nu(\omega)}. \tag{5.10}$$

VI. INITIAL CONDITIONS

To define our problem uniquely, we must determine the integration limit ω_0, and initial conditions for A^i_ν and $A^{\mathbf{k}}_\nu$, so that the physical initial conditions (2.4) are satisfied. The initial conditions for bound states and for the continuum are considered separately. Notice that the initial conditions are identical for $b=0$ and $b\neq0$, and we shall not distinguish between these two cases in this section.

A. Initial conditions for bound states

In order to set up initial conditions for Eqs. (5.4), we consider bound wave functions at large internuclear distances $R(t)\to\infty$. To this end, we replace τ in Eq. (4.1) by $\widetilde{R}(\tau)$ using

$$\tau=-\frac{1}{v\widetilde{R}(\tau)}, \tag{6.1}$$

that is exact for $b=0$ and asymptotic as $\tau\to0$ for $b\neq0$. Notice that the Fourier variable ω associated with the ''time'' variable τ is connected to the Fourier variable ε associated with the physical time t by

$$\omega=\varepsilon\widetilde{R}^2(\tau). \tag{6.2}$$

Then Eq. (4.1) becomes

$$\varphi^-_i(\tau,\mathbf{r}/\widetilde{R}(\tau))=\frac{1}{\sqrt{-2\pi i}}\widetilde{R}^2(\tau)\int_{-\infty}^{\infty}d\varepsilon \times\exp[-i\varepsilon\widetilde{R}(\tau)/v]\chi^-_i(\varepsilon\widetilde{R}^2(\tau),\mathbf{r}/\widetilde{R}(\tau)). \tag{6.3}$$

When $\widetilde{R}(\tau)\to\infty$, we can use asymptotic forms Eq. (5.7) for coefficients $B^i_\nu(\omega)$, and calculate the integral above by the stationary phase method. The rapidly varying phase is

$$f_\nu(\varepsilon)=\frac{\widetilde{R}^2(\tau)}{v}\int_{\varepsilon_0}^{\varepsilon}\frac{d\varepsilon'}{\rho_\nu(\varepsilon'\widetilde{R}^2(\tau))}-\frac{\varepsilon\widetilde{R}(\tau)}{v}, \tag{6.4}$$

where $\varepsilon_0=\omega_0/\widetilde{R}^2(\tau)$.

The stationary point $\mathcal{E}_\nu$ is found from the equation $df_\nu(\varepsilon)/d\varepsilon=0$, that gives

$$\rho_\nu(\mathcal{E}_\nu\widetilde{R}^2(\tau))=\widetilde{R}(\tau). \tag{6.5}$$

We see that the stationary point coincides with adiabatic energy at $R=\widetilde{R}(\tau)$ defined by Eq. (C9) in Appendix C. Calculating the integral in Eq. (6.4) by parts

$$f_\nu(\mathcal{E}_\nu)=\frac{\widetilde{R}^2(\tau)}{v}\left\{\frac{\varepsilon'}{\rho_\nu(\varepsilon'\widetilde{R}^2)}\right|_{\varepsilon_0}^{\mathcal{E}_\nu}-\frac{\mathcal{E}_\nu}{\widetilde{R}(\tau)} +\int_{\varepsilon_0}^{\mathcal{E}_\nu}\frac{\varepsilon'}{[\rho_\nu(\varepsilon'\widetilde{R}^2)]^2}\frac{d\rho_\nu}{d\varepsilon'}d\varepsilon'\Bigg\}, \tag{6.6}$$

we see that the upper limit of the first term is canceled exactly by the second term if we take into account Eq. (6.5), and the lower limit of the first term usually goes away since $\widetilde{R}(\tau)$ and $\rho_\nu(\varepsilon_0\widetilde{R}^2)\to\infty$. We change the integration variable from ε' to R using

$$R=\rho_\nu(\varepsilon'\widetilde{R}^2), \tag{6.7}$$

and notice that

$$\varepsilon'=\frac{[\rho_\nu]^{-1}(R)}{\widetilde{R}^2(\tau)}\equiv\frac{\varepsilon_\nu(R)}{\widetilde{R}^2(\tau)}\equiv\frac{R^2}{\widetilde{R}^2(\tau)}E_\nu(R), \tag{6.8}$$

where $\varepsilon_\nu(R)=R^2E_\nu(R)$ is the adiabatic energy in scaled coordinates, and $E_\nu(R)$ is the usual adiabatic energy without scaling. The phase at the stationary point now becomes

$$f_\nu(\mathcal{E}_\nu)=\frac{1}{v}\int_{\rho_\nu(\varepsilon_0\widetilde{R}^2)}^{\widetilde{R}(\tau)}E_\nu(R)dR \equiv-\int_{-T_0}^{t}E_\nu(t)dt\underset{\omega_0\to-\infty}{\to}-\int_{-\infty}^{t}E_\nu(t)dt. \tag{6.9}$$

Thus, setting $\omega_0\to-\infty$ one finds that the phase $f_\nu(\mathcal{E}_\nu)$ at the stationary point is identical to the adiabatic phase used in the initial conditions (2.4).

Taking integrals in Eq. (6.3) by the stationary phase method, we obtain

$$\varphi^-_i(\tau,\mathbf{r}/\widetilde{R}(\tau))=\sqrt{v}\sum_\nu A^i_\nu(-\infty)\frac{S_\nu(\mathcal{E}_\nu\widetilde{R}^2(\tau);\mathbf{r}/\widetilde{R}(\tau))}{\sqrt{-\dfrac{\partial\rho_\nu}{\partial\omega_\nu}}} \times\exp\left(-i\int_{-\infty}^{t}E_\nu(t)dt\right), \tag{6.10}$$

where $\omega_\nu=\mathcal{E}_\nu\widetilde{R}^2(\tau)$.

We perform the Solov'ev-Vinitsky transformation Eqs. (3.1), (3.2), and (3.3), and notice that, according to Eq. (C11) in Appendix C,

$$\Phi_\nu(R;\mathbf{r})=\frac{S_\nu(\mathcal{E}_\nu R^2;\mathbf{r}/R)}{\sqrt{-\partial\rho_\nu/\partial\omega_\nu}}, \tag{6.11}$$

to obtain the initial wave function in $\{t,\mathbf{r}\}$ space

$$\psi(t,\mathbf{r})=e^{i\gamma_{\rm trnsl}(\mathbf{r},t,\mathbf{v})}\sum_\nu A^i_\nu(-\infty)\Phi_\nu(R(t),\mathbf{r})e^{-i\int_{-\infty}^t E_\nu(t)dt}. \tag{6.12}$$

By inspection of Eq. (2.4) it is easy to see now that the appropriate initial condition for $A^i_\nu(\omega)$ is

$$A^i_\nu(-\infty)=\frac{1}{\sqrt{v}}a^i_\nu, \tag{6.13}$$

where a^i_ν is a constant given by Eq. (2.4).

B. Initial conditions for continuum states

Since we have explicitly extracted the free-electron motion in the continuum wave functions Eqs. (2.6), (3.10), and (4.9), initial conditions on the coefficients $A^{\mathbf{k}}_\nu(\omega)$ are determined by the orthogonality of $\psi_{\mathbf{k}}$ to all ψ_i. At large negative ω they are zero,

$$A^{\mathbf{k}}_\nu(-\infty)=0. \tag{6.14}$$

This simplicity of initial conditions comes at the expense of having inhomogeneous terms in Eq. (5.6).

VII. SUMMARY OF THE GENERAL THEORY

At this point the theory is complete. To find the transition amplitudes one proceeds as follows. In case of $b\neq 0$, first, it is necessary to solve the recurrence equation (5.4) to find the coefficients $B^i_\nu(\omega)$ for bound state initial conditions, or to solve Eq. (5.6) to obtain coefficients $B^{\mathbf{k}}_\nu(\omega)$ for the continuum initial conditions. Using expansions (5.1) for functions $\chi(\omega)$ it is straightforward now to obtain the transition amplitudes from Eq. (A16). For $b=0$ one solves differential equations (5.8) for bound states or (5.9) for the continuum to find the coefficients in expansions (5.1).

The case $b=0$ is different in that both discrete and continuum parts of the problem have to be considered. (For $b\neq 0$ the oscillator potential eliminates the continuum part.) In Sec. VIII we present applications of the theory for $b=0$ to emphasize the necessary modifications of the general theory in this important particular case.

VIII. APPLICATION: SPECTRA OF EJECTED ELECTRONS FOR HEAD-ON COLLISIONS

In this section we present an application of the general theory in the case $b=0$. There is no oscillator potential in this case, and all the potentials in the Schrödinger equation Eq. (3.5) go to zero at infinity. For this reason one has to distinguish between incoming and outgoing Sturmian functions for $\omega>0$ (see Appendix C). Short-range and Coulomb potentials will be considered.

A. Short-range potentials

When $Z_1=-Z_2$, the two-Coulomb-center potential becomes a short-range potential. Substituting Eqs. (4.9) and (5.1) with outgoing Sturmian functions into Eq. (4.5), we obtain the following expression for the transition amplitude:

$$T_{\mathbf{k},i}=\frac{i}{2\pi}\sum_\nu\int_{-\infty}^{\infty}d\omega B^i_{\nu'}(\omega)\int_{-\infty}^{\infty}d\omega' e^{-i(\omega-\omega')\tau}\times\left[\frac{1}{\sqrt{2\pi}v^{3/2}}\langle\mathbf{k}/v|G^{\rm in}(\omega')|S^{\rm out}_\nu(\omega)\rangle+\sum_{\nu'}B^{\mathbf{k}}_{\nu'}(\omega)\langle S^{\rm in}_{\nu'}(\omega')|S^{\rm out}_\nu(\omega)\rangle\right], \tag{8.1}$$

where we used $S^{\rm in}=(S^{\rm out})^*$ [see Eq. (C16)]. For short-range potentials the matrix elements $\langle S^{\rm in}_{\nu'}(\omega')|S^{\rm out}_\nu(\omega)\rangle$ and $\langle\mathbf{k}/v|G^{\rm in}(\omega')|S^{\rm out}_\nu(\omega)\rangle$ have first-order poles at $\omega=\omega'$ with residues $R_{\nu'\nu}(\omega)$ and $R^{(\rm G)}_\nu(\omega;\mathbf{k}/v)$, respectively. [See Eqs. (C18) and (C28) in Appendix C.] Thus we obtain

$$T_{\mathbf{k},i}=\sum_\nu\int_0^\infty d\omega B^i_\nu(\omega)\left[\frac{1}{\sqrt{2\pi}v^{3/2}}R^{(\rm G)}_\nu(\omega;\mathbf{k}/v)+\sum_{\nu'}B^{\mathbf{k}}_{\nu'}(\omega)R_{\nu'\nu}(\omega)\right]. \tag{8.2}$$

For short-range potentials the outgoing (incoming) Sturmian functions behave at large q as

$$S^{\rm out(in)}_\nu(\omega;\mathbf{q})\sim C^{\rm out(in)}_\nu(\omega)\,\frac{e^{\pm ipq}}{q}F^{\rm out(in)}_\nu(\omega,\hat{\mathbf{q}}), \tag{8.3}$$

where $C^{\rm out(in)}_\nu(\omega)$ are normalization constants $C^{\rm in}_\nu(\omega)=[C^{\rm out}_\nu(\omega)]^*$, and $F^{\rm out(in)}_\nu(\omega,\hat{\mathbf{q}})$ are normalized angular parts of Sturmian functions $F^{\rm in}_\nu(\omega,\hat{\mathbf{q}})=[F^{\rm out}_\nu(\omega,\hat{\mathbf{q}})]^*$:

$$\int d\hat{\mathbf{q}}\,F^{\rm out(in)}_\nu(\omega,\hat{\mathbf{q}})F^{\rm out(in)}_\nu(\omega,\hat{\mathbf{q}})=1. \tag{8.4}$$

Using Green's theorem and asymptotic forms of Sturmian functions Eq. (8.3), it is easy to find residues $R_{\nu\nu'}(\omega)$ of matrix elements $\mathcal{M}_{\nu\nu'}(\omega,\omega')$ at the pole $\omega=\omega'$:

$$\begin{aligned}R_{\nu\nu'}(\omega)&=\langle S^{\rm in}_\nu(\omega)|-V|S^{\rm out}_{\nu'}(\omega)\rangle[\rho^{\rm out}_{\nu'}(\omega)-\rho^{\rm in}_\nu(\omega)]\\&=\langle S^{\rm in}_\nu(\omega)|H_0|S^{\rm out}_{\nu'}(\omega)\rangle-\langle S^{\rm out}_{\nu'}(\omega)|H_0|S^{\rm in}_\nu(\omega)\rangle\\&=\frac{1}{2}\lim_{S\to\infty}\oint_S ds[S^{\rm in}_\nu(\omega;\mathbf{q})\nabla_{\mathbf{q}}S^{\rm out}_{\nu'}(\omega;\mathbf{q})-S^{\rm out}_{\nu'}(\omega;\mathbf{q})\nabla_{\mathbf{q}}S^{\rm in}_\nu(\omega;\mathbf{q})]\\&=ipC^{\rm out}_{\nu'}(\omega)C^{\rm in}_\nu(\omega)\int d\hat{\mathbf{q}}\,F^{\rm out}_{\nu'}(\omega,\hat{\mathbf{q}})F^{\rm in}_\nu(\omega,\hat{\mathbf{q}}).\end{aligned} \tag{8.5}$$

Residues $R^{(\rm G)}_{\nu\nu'}(\omega;\mathbf{k}/v)$ are found in the same manner as $R_{\nu\nu'}(\omega)$. Using the asymptotic forms of Green's function

$$G^{\rm out}(\omega;\mathbf{q},\mathbf{k}/v)\approx 2\frac{e^{ipq}}{q}\sum_{l=0}^{\infty} i^l j_l(pq')\sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{k}}/v)Y_{lm}(\hat{\mathbf{q}}), \tag{8.6}$$

where $Y_{lm}(\hat{\mathbf{q}})$ are spherical harmonics and $j_l(x)$ are spherical Bessel functions, we find

$$R_\nu^{(\rm G)}(\omega;\mathbf{k}/v)=ipC_\nu(\omega)\sum_{l=0}^{\infty} i^l j_l(pq') \times\sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{k}}/v)\int d\hat{\mathbf{q}}F_\nu^{\rm in}(\omega,\hat{\mathbf{q}})Y_{lm}(\hat{\mathbf{q}}). \tag{8.7}$$

Using the orthogonality of ψ_i and $\psi_{\mathbf{k}}$, which can be written as

$$\sum_\nu\int_0^\infty d\omega B_\nu^i(\omega)\left\{\frac{1}{\sqrt{2\pi}v^{3/2}}R_{\nu'}^{(\rm G)}(\omega;\mathbf{k}/v) +\sum_{\nu'}[B_{\nu'}^{\mathbf{k}}(\omega)]^* R_{\nu'\nu}(\omega)\right\}=0, \tag{8.8}$$

we can eliminate the first term associated with the plane wave in Eq. (8.2). Then the transition amplitude is

$$T_{\mathbf{k},i}=2\sum_\nu\sum_{\nu'}\int_0^\infty d\omega B_\nu^i(\omega)R_{\nu'\nu}(\omega)\,\mathrm{Im}\,B_{\nu'}^{\mathbf{k}}(\omega). \tag{8.9}$$

B. Coulomb potentials

From the asymptotic behavior of the functions χ [Eqs. (4.10) and (4.11)], it follows that the matrix element $\langle\chi_{\mathbf{k}}^+(\omega')|\chi_i^-(\omega)\rangle$ have only first-order poles at $\omega=\omega'$ and $\omega>0$ even though the matrix elements $\langle\mathbf{k}/v|G^{\rm in}(\omega')|S_{\nu'}^{\rm out}(\omega)\rangle$ and $\langle S_\nu^{\rm in}(\omega')|S_{\nu'}^{\rm out}(\omega)\rangle$ in Eq. (8.1) have more complicated singularities in two-Coulomb-center problems. This means that our solutions are good for finite q but must fail asymptotically. Such situation are readily treated by the Padé summation. In actual practice we use Padé summation to obtain an efficient algorithm. To this end we first write $\chi_I(\omega,\mathbf{q})$ [$\chi_I(\omega,\mathbf{q})$ denotes $\chi_i(\omega,\mathbf{q})$ or $\chi_{\mathbf{k}}^{\rm scat}(\omega,\mathbf{q})$] as a power-series expansions in spheroidal coordinates ($\xi=q_1+q_2$ and $\eta=q_1-q_2$) near $\xi=1$,

$$\chi_I(\omega,\mathbf{q})=\sum_\nu B_\nu^I(\omega)S_\nu(\omega;\mathbf{q}) =\underset{\xi\to1}{\to}\frac{2}{\xi+1}e^{ip(\xi-1)/2}\sum_s a_s^I(\omega,\eta,\phi)\left(\frac{\xi-1}{2}\right)^s, \tag{8.10}$$

where $a_s^I(\omega,\eta,\phi)$ are expansion coefficients and two Coulomb center Sturmian functions $S_\nu(\omega;\mathbf{q})$ are discussed in Appendix C4. The Padé summation [17] gives

$$\chi_I(\omega,\mathbf{q})\approx\frac{2}{\xi+1}e^{ip(\xi-1)/2}\frac{\sum_s^n c_s^I(\omega,\eta,\phi)(\xi-1)^s}{\sum_s^n d_s^I(\omega,\eta,\phi)(\xi-1)^s} \sim\frac{2}{\xi}e^{ip(\xi-1)/2}\frac{c_n^I(\omega,\eta,\phi)}{d_n^I(\omega,\eta,\phi)}, \tag{8.11}$$

where $c_n^I(\omega,\eta,\phi)$ and $d_n^I(\omega,\eta,\phi)$ are Padé coefficients. Thus we construct asymptotic constants Eqs. (4.10) and (4.11) as $C_I(\omega,\hat{\mathbf{q}})\approx\exp(ip/2)c_n^I/d_n^I$.

The transition amplitude Eq. (4.5) becomes

$$T_{\mathbf{k},i}=\int_0^\infty \mathrm{Re}\,s_{\omega=\omega'}\langle\chi_{\mathbf{k}}^+(\omega')|\chi_i^-(\omega)\rangle d\omega, \tag{8.12}$$

with

$$\mathrm{Re}\,s_{\omega=\omega'}\langle\chi_{\mathbf{k}}^+(\omega')|\chi_i^-(\omega)\rangle =\sqrt{2\omega}\int d\hat{\mathbf{q}}C_i(v,\omega,\hat{\mathbf{q}})[C_{\mathbf{k}}(v,\omega,\hat{\mathbf{q}}) -C_{\mathbf{k}}^*(-v,\omega,-\hat{\mathbf{q}})]. \tag{8.13}$$

In Eq. (8.13) we used the orthogonality of ψ_i and $\psi_{\mathbf{k}}$ to eliminate the plane-wave contribution.

IX. RESULTS AND DISCUSSION

The actual solution of the problem can be divided into three stages. First, we truncate the coupled equations (5.8) and (5.9) at $N\approx10$, and solve them with the initial conditions given by Eqs. (6.13) and (6.14) to find the coefficients $A_\nu^i(\omega)$ and $A_\nu^{\mathbf{k}}(\omega)$ for $\omega<0$. Since for $\omega<0$ T Sturmian functions form a complete set, the solution of these equations gives the values of $A_\nu^i(\omega)$ and $A_\nu^{\mathbf{k}}(\omega)$ for the T Sturmian functions at $\omega=0$. As we have shown for $\omega>0$ the complete set contains both T and S Sturmian functions. In order to preserve continuity of the solution the coefficients $A_\nu^i(\omega)$ and $A_\nu^{\mathbf{k}}(\omega)$ of the S Sturmian functions should equal zero at $\omega=0$. On the second stage of solution we use the computed values of $A_\nu^i(\omega)$ and $A_\nu^{\mathbf{k}}(\omega)$ for the T Sturmian functions at $\omega=0$ and zero initial conditions for the S Sturmian functions to solve Eqs. (5.8) from $\omega=0$ to $\omega=+\infty$. Notice that the coupling terms are of order ω^{-1} near $\omega=0$, and the differential equations (5.8) and (5.9) are of first order. The solutions near $\omega=0$, therefore have the form of a Frobenius rather than a Taylor series. As an alternative to using a Frobenius solution with a large basis set we can exploit the connection between one- and two-Coulomb-center functions near $\omega=0$, to solve the coupled equations for small ω. We construct $C_i(\omega,\hat{\mathbf{q}})$ and $C_{\mathbf{k}}(\omega,\hat{\mathbf{q}})$ using the Padé summation [17]. The sequence of Padé approximants converges fairly rapidly. It is interesting to notice that for $v=0.4$ a.u. the one Sturmian approximation already gives accurate enough results (within 10%).

Three spectra of electrons ejected in collisions of protons with hydrogen atoms are displayed in Figs. 1–3. Two different kinds of Sturmian functions are responsible for these two

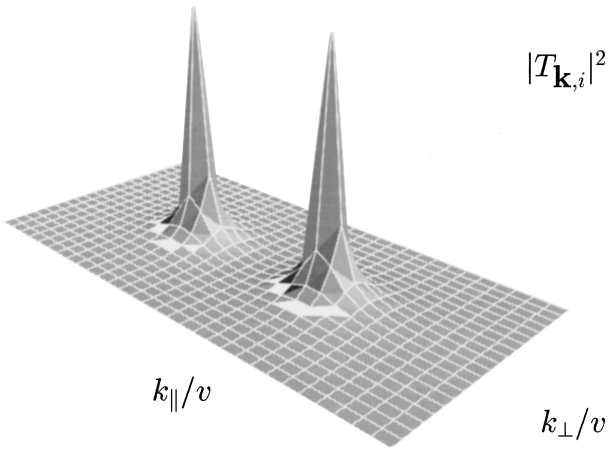

FIG. 1. Differential ionization probabilities $|T_{\mathbf{k},i}|^2$ at $v=0.4$ a.u. and $b=0$ for the S promotion of the $2p\sigma$ state.

types of spectra. Figure 1 shows a spectrum related to the S promotion for $v=0.4$ a.u. The spectrum has two cusp peaks at $k_\perp=0$ and $k_\parallel=\pm v/2$ in the center-of-mass frame. That the S-promotion mechanism gives cusp electrons can be understood from the corresponding classical trajectories given in Ref. [18]. These authors show that the S-promotion classical orbits circle both protons an infinite number of times. Since the electron spends a large fraction of its time near the protons, the electron distribution peaks at $\mathbf{k}=\pm\mathbf{v}/2$. The energy distribution of the fast electrons is exponential. Figures 2 and 3 show a spectrum related to the T promotion of $2p\pi$ and $1s\sigma$ states, respectively, for $v=0.4$ a.u. The two peaks at zero center-of-mass velocity in Fig. 2 are associated with the π symmetry of the T_{01} promotion. This agrees with calculations reported in Ref. [19]. The distribution in Fig. 2 corresponds to $R_{\text{ion}}\approx 110$ a.u., in good agreement with $R_{\text{ion}}=50/v$ used in Ref. [19].

Standard low-energy theories employing perturbed stationary states [13] cannot calculate energy and angular distributions of electrons, and especially cannot obtain the continuum capture cusp which should be present in the spectra. Previous calculations of total cross sections have identified two ionization mechanisms [20,21] at low-energy collisions, called T promotion and S promotion, but have not been able

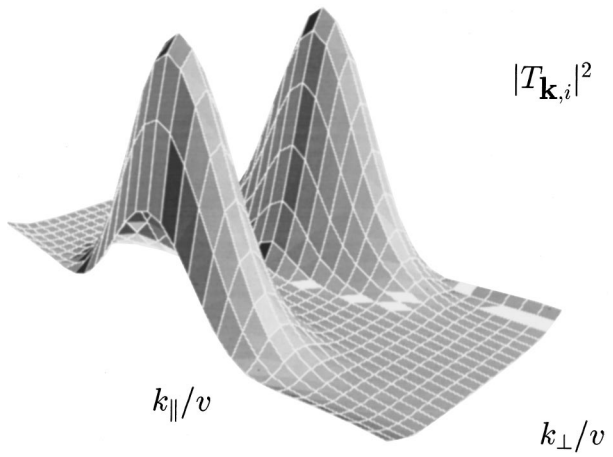

FIG. 2. Same as Fig. 1 for the T promotion of the $2p\pi$ state.

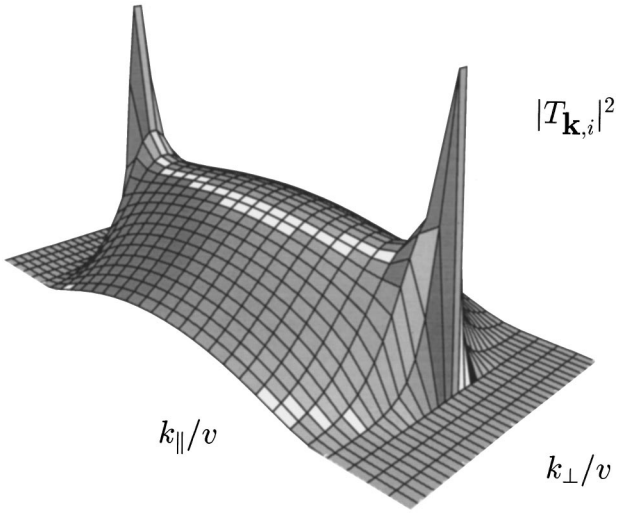

FIG. 3. Same as Fig. 1 for the T promotion of the $1s\sigma$ state.

to compute the corresponding electron distributions on an *ab initio* basis.

The electrons promoted to the continuum via a T promotion are called saddle-point electrons. This reflects the fact that the electrons are picked up in the saddle region of the potential energy and promoted to the continuum as the two charges recede from each other. The electrons locate in space at the saddle point between the nuclei. For equal charges, their velocities $\mathbf{k}$ are distributed around one-half of the velocity of the incoming particles. Recent calculations [22,23] obtain such a distribution for saddle-point electrons, but employ an adjustable parameter R_{ion}, where adiabatic and diabatic wave functions are matched. In the present calculations we eliminate this arbitrary parameter.

The S-promotion electrons are associated with classical, periodic, unstable trajectories which represent electron motion along the axis joining the charges [18]. The kinetic energy of electrons on these trajectories increases when the charges approach each other. The increase of kinetic energy leads to ionization even when the relative velocity is insufficient to ionize electrons in a single binary collision. A simple analog of this mechanism is the acceleration of elastic balls bouncing between two walls that slowly approach each other. Present ''hidden crossing'' theory [20,21] cannot compute the complete distribution of these electrons.

Our formulation in terms of Sturmian eigenfunctions presents a complete *ab initio* theory of ionization in ion-atom collisions with *arbitrary* velocity, and especially in the low- and intermediate-energy regions ($v<1$ a.u.). Various Born approximations usually break down at low and intermediate energies, and neither ''hidden crossing'' nor close-coupling theories are able to calculate complete electron spectra in their regions of validity. First calculations by the Sturmian technique show that two previously identified ionization mechanisms give dramatically different electron distributions. The T-promotion mechanism gives a peak at the center-of-mass velocity, equal to $v/2$ in lab frame, as in earlier calculations, but without arbitrary adjustable parameters. The S-promotion mechanism gives rise to two cusps where electron velocities match the ion velocities. Our numerical calculations provide a solid confirmation of the qualitative considerations presented above. These theoretical results can

be used to interpret measured electron distributions in terms of T and S mechanisms.

While our calculations have been carried out in detail only for $b=0$, the results may also be used, in lowest order in v, for $b\neq 0$, since the terms involving b in Eq. (3.5) vanish in lowest order. Terms of higher order may also be kept so that the solutions of the difference equation (5.4) become relevant. Almost identical difference equations have been used to treat ionization in the hyperspherical representation. Here it was shown that the hidden crossing theory for ionization via the T-promotion series, computed in Ref. [24], emerges from the Sturmian theory even for $b\neq 0$. In the present manuscript we have computed both the S- and T-promotion distributions essentially exactly for $b=0$. We can anticipate that the T distributions, thus obtained, will remain even for $b\neq 0$, but cannot project how the S-promotion mechanism will emerge in that case.

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APPENDIX A: TRANSITION AMPLITUDES IN FOURIER SPACE

In this appendix we derive a very general expression for the transition amplitude in $\{\omega,\mathbf{q}\}$ space. It will be shown that causality imposes very significant restrictions on the transition amplitude, and the final result can be reduced to the calculation of a residue at the pole of a certain function.

Two cases will be considered: (i) the general case when zero internuclear distance R is never reached; and (ii) the special case when there is no interaction between the nuclei and they can come infinitely close together. In practice the second case can be realized mostly for straight-line trajectories and zero impact parameter. Although in both cases the final expression is essentially the same, the zero-impact-parameter case requires somewhat special treatment.

We look for the transition amplitude in $(t,\mathbf{r})$ space in the form

$$T_{12}=\langle \psi_2^+(t)|\psi_1^-(t)\rangle, \tag{A1}$$

where the indices {1,2} are associated with some initial conditions, the index ''$-$'' corresponds to propagation in the positive direction in time, and the index ''$+$'' means that the function is counterpropagated in time. It is important to notice here that although the wave function is calculated at a certain moment of time t, the transition amplitude is actually independent of time. The counterpropagating function ψ^+ is connected to ψ^- by the well-known formula

$$\psi^+(t,\mathbf{r})=[\psi^-(t,-\mathbf{r})]^*. \tag{A2}$$

According to the Solov'ev-Vinitsky transformation, we write

$$\psi^-(t,\mathbf{r})=\frac{1}{R^{3/2}(t)}\exp\left\{\frac{i}{2R(t)}\frac{dR}{dt}r^2\right\}\varphi^-(\tau(t),\mathbf{r}/R(t)), \tag{A3}$$

where $\tau(t)$ is defined by Eq. (3.2). According to Eq. (A2), for ψ^+ we obtain [assuming for simplicity that $R(-t)=R(t)$]

$$\psi^+(t,\mathbf{r})=\frac{1}{R^{3/2}(t)}\exp\left\{\frac{i}{2R(t)}\frac{dR}{dt}r^2\right\}\times[\varphi^-(\tau(-t),-\mathbf{r}/R(t))]^*. \tag{A4}$$

Noticing that

$$\tau(-t)=\tau_{\max}-\tau(t), \tag{A5}$$

it is easy to obtain the following expression for the transition amplitude:

$$T_{12}=\int d^3\mathbf{q}\ \varphi_2^-(\tau_{\max}-\tau,-\mathbf{q})\varphi_1^-(\tau,\mathbf{q}), \tag{A6}$$

where

$$\tau_{\max}=\int_{-\infty}^{\infty}\frac{dt'}{R^2(t')}. \tag{A7}$$

In order to separate τ and $\mathbf{q}$ dependencies, we chose to work in the Fourier space

$$\varphi^-(\tau,\mathbf{q})=\frac{1}{\sqrt{-2\pi i}}\int_{-\infty}^{\infty}d\omega\ \exp(-i\omega\tau)\chi(\omega,\mathbf{q}). \tag{A8}$$

The transition amplitude now becomes

$$T_{12}=\frac{i}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}d\omega\ d\omega'\exp[-i(\omega-\omega')\tau]\times\exp(-i\omega'\tau_{\max})\int d^3\mathbf{q}\chi_2(\omega',-\mathbf{q})\chi_1(\omega,\mathbf{q}). \tag{A9}$$

Notice that in this case there is no continuum (since there is an oscillator potential), and no distinction between ''in'' and ''out'' functions is needed.

To make the transition amplitude properly causal we have to define it for all τ

$$T_{12}(\tau)=\begin{cases}0 & \text{if } \tau<0\\ T_{12} & \text{if } \tau>0 \text{ (independent of } \tau).\end{cases} \tag{A10}$$

We are now going to show that the condition above can be satisfied if, and only if, the integrand in Eq. (A9) has a simple pole at $\omega=\omega'$. To this end we rewrite Eq. (A9) in the form

$$T_{12}(\tau)=\frac{i}{2\pi}\int_{-\infty}^{\infty}d\Omega\ \exp(-i\Omega\tau)\int_{-\infty}^{\infty}F(\Delta\omega,\omega')d\omega', \tag{A11}$$

where we changed the variables $\Delta\omega=\omega-\omega'$ and introduced a new function

$$F(\Delta\omega,\omega')=\exp(-i\omega'\tau_{\max})\int d^3\mathbf{q}\ \chi_2(\omega',-\mathbf{q}) \times\chi_1(\omega'+\Delta\omega,\mathbf{q}). \tag{A12}$$

Performing the inverse Fourier transformation, we obtain

$$\int_{-\infty}^{\infty}F(\Delta\omega,\omega')d\omega'=-i\int_{-\infty}^{\infty}d\tau\ T_{12}(\tau)\exp(i\Delta\omega\tau). \tag{A13}$$

The integral on the right-hand side is well defined in the upper half-plane of the complex variable $\Delta\omega$, and we replace

$$\Delta\omega\rightarrow\Delta\omega+i\varepsilon,\quad \varepsilon>0. \tag{A14}$$

It is now straightforward to obtain

$$\int_{-\infty}^{\infty}F(\Delta\omega+i\varepsilon,\omega')d\omega'=\frac{T_{12}}{(\Delta\omega+i\varepsilon)}, \tag{A15}$$

and we deduce that the transition amplitude is proportional to the residue at $\Delta\omega=0$ of the integral on the left-hand side of Eq. (A15),

$$T_{12}=\mathrm{Re}\ s_{\Delta\omega=0}\int_{-\infty}^{\infty}F(\Delta\omega,\omega')d\omega'. \tag{A16}$$

Thus it has been proved that if the transition amplitude is causal as defined by Eq. (A10), then the integrand in Eq. (A9) has a simple pole. The proof of the inverse statement is elementary, and we shall not give it here. The important result of this section is the formula for the transition amplitude Eq. (A16).

APPENDIX B: INVARIANCE OF STURMIAN MATRIX ELEMENTS FOR NONZERO IMPACT PARAMENTER

In this appendix we illustrate the invariance of the Sturmian theory to shifts of the coordinate system along the internuclear axis. Our discussion follows closely the demonstration in Ref. [11].

The differential equation for the Sturmian functions is

$$[\tfrac{1}{2}\mathbf{p}^2+\rho_\nu(\omega)V(\mathbf{q})+\Omega^2q^2+\Omega L_y]S_\nu(\omega;\mathbf{q})=\omega S_\nu(\omega;\mathbf{q}) \tag{B1}$$

which can be written in the magnetic-field form

$$[\tfrac{1}{2}(\mathbf{p}-\mathbf{q}\times\boldsymbol{\Omega})^2+\rho_\nu(\omega)V(\mathbf{q})+\tfrac{1}{2}\Omega^2q_y^2]S_\nu(\omega;\mathbf{q}) =\omega S_\nu(\omega;\mathbf{q}). \tag{B2}$$

A shift of the origin along the internuclear axis $\mathbf{r}=\mathbf{r}'+\alpha R(t)\hat{\mathbf{z}}$ corresponds to the transformation in scaled coordinates,

$$\mathbf{q}=\mathbf{q}'+\alpha\hat{\mathbf{z}}, \tag{B3}$$

where α is a constant that defines the origin of the new coordinate frame. The new Schrödinger equation is

$$[\tfrac{1}{2}(\mathbf{p}'-\mathbf{q}'\times\boldsymbol{\Omega}-\alpha\hat{\mathbf{z}}\times\boldsymbol{\Omega})^2+\rho_\nu(\omega)V(\mathbf{q}') +\tfrac{1}{2}\Omega^2q_y'^2]S_\nu(\omega;\mathbf{q}'+\alpha\hat{\mathbf{z}})=\omega S_\nu(\omega;\mathbf{q}'+\alpha\hat{\mathbf{z}}). \tag{B4}$$

The gauge transformation

$$S_\nu(\omega;\mathbf{q}'+\alpha\hat{\mathbf{z}})=\exp[i\alpha\hat{\mathbf{z}}\times\boldsymbol{\Omega}\cdot\mathbf{q}']S_\nu(\omega;\mathbf{q}') \tag{B5}$$

restores the original form of the equation defining $S_\nu(\omega;\mathbf{q})$,

$$[\tfrac{1}{2}(\mathbf{p}'-\mathbf{q}'\times\boldsymbol{\Omega})^2+\rho_\nu(\omega)V(\mathbf{q}')+\tfrac{1}{2}\Omega^2q_y'^2]S_\nu(\omega;\mathbf{q}') =\omega S_\nu(\omega;\mathbf{q}'). \tag{B6}$$

with $\mathbf{q}'$ replacing $\mathbf{q}$. Therefore we have

$$S_\nu(\omega;\mathbf{q}'+\alpha\hat{\mathbf{z}})=\exp[i\alpha\hat{\mathbf{z}}\times\boldsymbol{\Omega}\cdot\mathbf{q}']S_\nu(\omega;\mathbf{q}'), \tag{B7}$$

while the dual transforms as

$$\widetilde{S}_\nu(\omega;\mathbf{q}'+\alpha\hat{\mathbf{z}})=\exp[-i\alpha\hat{\mathbf{z}}\times\boldsymbol{\Omega}\cdot\mathbf{q}']\widetilde{S}_\nu(\omega;\mathbf{q}'). \tag{B8}$$

Even though the Sturmian functions change by a phase factor, the matrix elements in Eq. (5.4) remain unchanged since the phase factor is independent of ω and cancels in forming the product of a Sturmian and a dual.

APPENDIX C: REVIEW OF STURMIAN THEORY

1. Analytic properties of Sturmian functions and relation between Sturmian and scaled adiabatic sets

According to Demkov [25], an infinite set of adiabatic eigenvalues $\varepsilon_\nu(R)$ represent different sheets of the same analytic function $\varepsilon(R)$ on a multisheeted Riemann surface. Recall that a Riemann surface for a function is defined as a surface on which the function is single valued. On the real axis, the value of the function on the nth sheet is equal to the energy eigenvalue $\varepsilon_\nu(R)$, by construction. At complex R different sheets join at square root branch points R_b, so that, in the neighborhood of R_b, one has $\varepsilon(R)\propto\sqrt{R-R_b}$. For such functions it is possible to construct a Riemann surface by plotting Re $\varepsilon_\nu(R)$ vs R. The resulting surface is one on which $\varepsilon(R)$ is single valued. Furthermore, the separation between the sheets now gives additional information not normally included in the definition of the Riemann surface, namely, the intersection of this Riemann surface with a plane passing through the real axis and perpendicular to the R plane gives the multiplicity of potential curves $\varepsilon_\nu(R)$. On the real R axis the function $\varepsilon(R)$ is equal to a ''scaled'' adiabatic energy eigenvalue $\varepsilon_\nu(R)$ defined by the eigenvalue equation

$$[H_0(\mathbf{q})+RV(\mathbf{q})]\varphi_\nu(R;\mathbf{q})=\varepsilon_\nu(R)\varphi_\nu(R;\mathbf{q}). \tag{C1}$$

The Riemann surface also defines a universal adiabatic eigenfunction $\varphi(R;\mathbf{q})$ for all complex values of R. Adiabatic functions $\varphi_\nu(R;\mathbf{q})$ satisfy boundary conditions

$$\frac{\partial \varphi_\nu(R;\mathbf{q})}{\partial q}+\sqrt{-2\varepsilon_\nu(R)}\,\varphi_\nu(R;\mathbf{q})\sim 0, \quad \text{as } q\to\infty, \tag{C2}$$

which correspond to the Jost matrix. Some of the adiabatic energy eigenvalues $\varepsilon_\nu(R)$ on the real R axis may be complex, and the corresponding eigenfunctions $\varphi_\nu(R;\mathbf{q})$ exponentially increase as $q\to\infty$. This means that usual boundary conditions $\varphi(R;\mathbf{q})\sim 0$ as $q\to\infty$ define functions only on a small part of the Riemann surface with R close to the real axis.

The inverse function $\rho(\omega)$, which can be found from the equation

$$\varepsilon[\rho(\omega)]=\omega, \tag{C3}$$

is defined on its Riemann surface for all ω [7]. In analogy to the adiabatic case one defines a universal Sturmian eigenfunction $S(\omega;\mathbf{q})$ on the Riemann surface of $\rho(\omega)$. Different sheets of the Riemann surface are joined together at square-root branch points ω_b in the complex plane of ω. On the real ω axis, the value of the function on the nth sheet is equal to the Sturmian eigenvalues $\rho_\nu(\omega)$. These eigenvalues are associated with the Sturm-Liouville problem

$$[H_0(\mathbf{q})+\rho_\nu(\omega)V(\mathbf{q})]S_\nu(\omega;\mathbf{q})=\omega S_\nu(\omega;\mathbf{q}), \tag{C4}$$

with boundary conditions defined by the *parameter* ω,

$$\frac{\partial S_\nu(\omega;\mathbf{q})}{\partial q}+\sqrt{-2\omega}\,S_\nu(\omega;\mathbf{q})\sim 0, \quad \text{as } q\to\infty. \tag{C5}$$

One of the most important differences between adiabatic and Sturmian functions should be pointed out here: it is essential that Sturm-Liouville boundary conditions Eq. (C5) are independent of Sturmian eigenvalues $\rho_\nu(\omega)$. In other words, given *any* ω in Eq. (C5) it is possible to find a corresponding eigenvalue $\rho_\nu(\omega)$. In contrast, boundary conditions for adiabatic functions Eq. (C2) depend explicitly on adiabatic eigenvalues $\varepsilon_\nu(R)$, and, therefore, solutions of adiabatic problems require self-consistency between eigenvalues and boundary conditions. This fact makes Sturmian basis sets much more versatile than adiabatic ones.

Although adiabatic and Sturmian basis sets are very different, they are closely related. Comparison of Eqs. (C1) and (C4) shows that adiabatic eigenfunctions $\varphi_\nu(R;\mathbf{q})$ are, apart from normalization constants, just the Sturmian functions $S(\omega;\mathbf{q})$ evaluated at $\omega=\varepsilon_\nu(R)$:

$$\varphi_\nu(R;\mathbf{q})=N_\nu(R)S(\varepsilon_\nu(R);\mathbf{q}). \tag{C6}$$

The particular sheet of the Riemann surface $\rho(\omega)$ to calculate the function $S(\varepsilon_\nu(R);\mathbf{q})$ on should be chosen to satisfy the condition

$$\rho(\varepsilon_\nu(R))=R. \tag{C7}$$

If both R and $\varepsilon_\nu(R)$ are real, one can assign indices ν to different branches of the universal function $S(\varepsilon_\nu(R);\mathbf{q})$, and the relation between adiabatic and Sturmian functions becomes more explicit,

$$\varphi_\nu(R;\mathbf{q})=N_\nu(R)S_\nu(\varepsilon_\nu(R);=\mathbf{q}), \tag{C8}$$

where Sturmian branch index ν is chosen so that

$$\rho_\nu(\varepsilon_\nu(R))=R \tag{C9}$$

is satisfied. This form [Eqs. (C8) and (C9)] is very useful when establishing the correspondence between *bound* adiabatic states and Sturmian functions. However, when *quasistationary* states are involved one should use the more general prescription Eqs. (C6) and (C7).

Sturmian eigenfunctions are normalized according to

$$\langle S_\nu(\omega)|-V|S_{\nu'}(\omega)\rangle=-\int S_\nu(\omega;\mathbf{q})V(\mathbf{q})S_{\nu'}(\omega;\mathbf{q})d^3q = \delta_{\nu\nu'}. \tag{C10}$$

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. (C10). The potential is diagonal in the Sturmian representation. Since the potentials $V(\mathbf{q})$ 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. Sturmian normalization constants are [6]

$$N_\nu(R)=\left(-\frac{\partial\varepsilon_\nu(R)}{\partial R}\right)^{1/2}. \tag{C11}$$

There is also a very interesting analogy in behavior of coupling matrix elements calculated in adiabatic and Sturmian bases in the vicinity of branch points R_c and ω_b, respectively. It has been shown [26] that the adiabatic matrix elements have poles at $R=R_b$ with residues $\pm i/4$ independent of R_c,

$$\left\langle \varphi_\nu(R)\left|\frac{\partial}{\partial R}\right|\varphi_{\nu'}(R)\right\rangle\approx\frac{\pm\frac{i}{4}}{R-R_b}, \quad R\approx R_b. \tag{C12}$$

Similar considerations applied to the Sturmian case show that the Sturmian matrix elements also have poles at ω_b with exactly the same residue as in the adiabatic case,

$$\left\langle S_\nu(\omega)\left|-V\frac{\partial}{\partial\omega}\right|S_{\nu'}(\omega)\right\rangle=\frac{\langle S_\nu(\omega)|S_{\nu'}(\omega)\rangle}{\rho_\nu(\omega)-\rho_{\nu'}(\omega)} \approx\frac{\pm\frac{i}{4}}{\omega-\omega_b}, \quad \omega\approx\omega_b. \tag{C13}$$

2. Positive energy Sturmian functions

Both incoming and outgoing Sturmian functions at positive ω are analytic continuations of the same set of Sturmian functions at negative ω. (i) Outgoing Sturmian functions satisfying outgoing wave boundary conditions,

$$\frac{\partial S_\nu^{\text{out}}(\omega;\mathbf{q})}{\partial q}-i\sqrt{2\omega}\,S_\nu^{\text{out}}(\omega;\mathbf{q})\sim 0 \quad \text{as } q\to\infty. \tag{C14}$$

(ii) Incoming Sturmian functions satisfying incoming wave boundary conditions,

$$\frac{\partial S_\nu^{\rm in}(\omega;\mathbf{q})}{\partial q}+ipS_\nu^{\rm in}(\omega;\mathbf{q})\sim 0 \quad \text{as} \quad q\to\infty. \tag{C15}$$

Both boundary conditions (C14) and (C15) are obtained by analytic continuation to $\omega>0$ of the boundary conditions (C5). For real ω these two sets of Sturmian functions are complex conjugate,

$$\rho_\nu^{\rm in}(\omega)=[\rho_\nu^{\rm out}(\omega)]^* \quad \text{and} \quad S_\nu^{\rm in}(\omega;\mathbf{q})=[S_\nu^{\rm out}(\omega;\mathbf{q})]^*. \tag{C16}$$

The overlap integrals between incoming and outgoing Sturmian functions,

$$\langle S_\nu^{\rm in}(\omega)|S_{\nu'}^{\rm out}(\omega')\rangle=\frac{\rho_\nu^{\rm in}(\omega)-\rho_{\nu'}^{\rm out}(\omega')}{\omega-\omega'}\langle S_\nu^{\rm in}(\omega)|-V|S_{\nu'}^{\rm out}(\omega')\rangle, \tag{C17}$$

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,

$$R_{\nu\nu'}(\omega)\equiv \mathrm{Re}\, s_{\omega\to\omega'}\mathcal{M}_{\nu\nu'}(\omega,\omega')=[\rho_\nu^{\rm in}(\omega)-\rho_{\nu'}^{\rm out}(\omega)]\times\langle S_\nu^{\rm in}(\omega)|-V|S_{\nu'}^{\rm out}(\omega)\rangle. \tag{C18}$$

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

$$S_\nu^{\rm in}(\omega,\mathbf{q})=\sum_{\nu'}\ \frac{R_{\nu\nu'}(\omega)}{\rho_{\nu'}^{\rm in}(\omega)-\rho_\nu^{\rm out}(\omega)}S_{\nu'}^{\rm out}(\omega,\mathbf{q}), \tag{C19}$$

which converges, but not absolutely.

3. Sturmian expansions of Green's functions

The Green's functions $G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')\equiv\langle\mathbf{q}|G^{\rm out(in)}(\omega)|\mathbf{q}'\rangle$, where $G^{\rm out(in)}=(H_0(\mathbf{q})-\omega\pm i\varepsilon)^{-1}$, are solutions of equations

$$[H_0(\mathbf{q})-\omega]G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')=\delta(\mathbf{q}-\mathbf{q}'), \tag{C20}$$

with outgoing (incoming) boundary conditions for $G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')$:

$$\frac{\partial G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')}{\partial q}\mp ipG^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')\sim 0, \quad \text{as} \quad q\to\infty. \tag{C21}$$

The outgoing (incoming) Green's functions of $H_0(\mathbf{q})=-\frac{1}{2}\nabla_{\mathbf{q}}^2$ in Eq. (C27) are free-particle Green's functions,

$$G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')=\frac{1}{2\pi}\frac{\exp(\pm ip|\mathbf{q}-\mathbf{q}'|)}{|\mathbf{q}-\mathbf{q}'|}. \tag{C22}$$

Overlap integrals with Green's functions have the same structure as the Sturmian overlap integrals

$$\langle\mathbf{q}|G^{\rm out(in)}(\omega)G^{\rm out}(\omega')|\mathbf{q}'\rangle=\frac{G^{\rm out(in)}(\omega;\mathbf{q},\mathbf{q}')-G^{\rm out}(\omega';\mathbf{q},\mathbf{q}')}{\omega-\omega'}. \tag{C23}$$

Equation (C23) shows, that at $\omega=\omega'$ overlap integrals $\langle\mathbf{q}|G^{\rm out}(\omega)G^{\rm out}(\omega)|\mathbf{q}'\rangle$ are finite:

$$\langle\mathbf{q}|G^{\rm out}(\omega)G^{\rm out}(\omega)|\mathbf{q}'\rangle=\frac{\partial G^{\rm out}(\omega;\mathbf{q},\mathbf{q}')}{\partial\omega}, \tag{C24}$$

and integrals $\langle\mathbf{q}|G^{\rm in}(\omega)G^{\rm out}(\omega')|\mathbf{q}'\rangle$ have a first-order pole at $\omega=\omega'$ with the residue

$$\mathrm{Re}\, s_{\omega\to\omega'}\langle\mathbf{q}|G^{\rm in}(\omega)G^{\rm out}(\omega')|\mathbf{q}'\rangle=G^{\rm in}(\omega;\mathbf{q},\mathbf{q}')-G^{\rm out}(\omega;\mathbf{q},\mathbf{q}'). \tag{C25}$$

To find Sturmian expansions of outgoing and incoming Green's functions, we consider matrix elements

$$\langle\mathbf{q}'|G^{\rm out(in)}(\omega)V|S_\nu^{\rm out}(\omega')\rangle=\frac{1}{\rho_\nu^{\rm out}(\omega')}[S_\nu^{\rm out}(\omega';\mathbf{q}')+(\omega-\omega')\times\langle\mathbf{q}'|G^{\rm out(in)}(\omega)|S_\nu^{\rm out}(\omega')\rangle]. \tag{C26}$$

For short-range potentials the overlap integrals $\langle\mathbf{q}'|G^{\rm out}(\omega)|S_\nu^{\rm out}(\omega)\rangle$ are finite, and Sturmian expansions of the outgoing Green's functions,

$$G^{\rm out}(\omega;\mathbf{q},\mathbf{q}')=\sum_\nu\ \frac{S_\nu^{\rm out}(\omega;\mathbf{q}')}{\rho_\nu^{\rm out}(\omega)}S_\nu^{\rm out}(\omega;\mathbf{q}), \tag{C27}$$

contain only outgoing waves (same for incoming waves) [27].

The overlap integrals $\langle\mathbf{q}'|G^{\rm in}(\omega)|S_\nu^{\rm out}(\omega')\rangle$ also have a first-order pole at $\omega=\omega'$ with residue

$$R_\nu^{(\rm G)}(\omega;\mathbf{q}')\equiv\mathrm{Re}\, s_{\omega\to\omega'}\langle\mathbf{q}'|G^{\rm in}(\omega)|S_\nu^{\rm out}(\omega')\rangle. \tag{C28}$$

The residue $R_\nu^{(\rm G)}(\omega;\mathbf{q}')$ can be expanded in terms of outgoing Sturmian functions,

$$R_\nu^{(\rm G)}(\omega;\mathbf{q}')=\sum_{\nu'}\ \frac{R_{\nu\nu'}(\omega)}{\rho_{\nu'}^{\rm out}(\omega)}S_{\nu'}^{\rm out}(\omega;\mathbf{q}'). \tag{C29}$$

4. Two-Coulomb-center Sturmian functions

The two-Coulomb-center Sturmian basis set is defined by

$$\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2+\rho_\nu\left(-\frac{Z_1}{q_1}-\frac{Z_2}{q_2}\right)\right]S_\nu(\omega;\mathbf{q})=\omega S_\nu(\omega;\mathbf{q}), \tag{C30}$$

where $q_i=r_i/R$.

This equation admits separation of variables in prolate spheroidal coordinates,

$$\xi = q_1 + q_2, \quad \eta = q_1 - q_2, \quad \phi = \arctan\left(\frac{x}{y}\right),$$
$$1 \leq \xi < \infty, \quad -1 \leq \eta \leq 1, \quad 0 \leq \phi < 2\pi,$$

where x and y are the Cartesian coordinates. Substituting the wave function

$$S(\omega;\mathbf{q}) = C(\omega)G(\xi)F(\eta)\exp(im\phi) \tag{C31}$$

into Eq. (C30) gives the set of differential equations [28]

$$\left[\frac{1}{\xi^2-1}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi} - \frac{\lambda_\xi}{\xi^2-1} + \frac{\omega}{2} + \rho\frac{(Z_1+Z_2)\xi}{\xi^2-1} - \frac{m^2}{(\xi^2-1)^2}\right]G(\xi) = 0, \tag{C32}$$

$$\left[\frac{1}{1-\eta^2}\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta} + \frac{\lambda_\eta}{1-\eta^2} + \frac{\omega}{2} + \rho\frac{(Z_1-Z_2)\eta}{1-\eta^2} - \frac{m^2}{(1-\eta^2)^2}\right]F(\eta) = 0, \tag{C33}$$

where $C(\omega)$ is a normalization factor and λ is a separation constant.

Equations (C32) and (C33) with the boundary conditions

$$|G(\pm 1)| < \infty, \quad |F(1)| < \infty, \quad \frac{\partial F(\xi)}{\partial \xi} - i\sqrt{2\omega}F(\xi) \underset{\xi\to\infty}{\to} 0 \tag{C34}$$

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 by solving the equation

$$\lambda_\xi(\rho,\omega) = \lambda_\eta(\rho,\omega). \tag{C35}$$

According to the general Sturm-Liouville theory, when $\omega < 0$, the Sturmian eigenvalues and eigenfunctions are real, and the number of nodes of quasiradial wave functions (n_ξ) and quasiangular wave functions (n_η) are conserved when the parameter ω varies. The Sturmian functions will be classified according to the united-atom spherical quantum numbers $\nu = (n,l,m)$. These numbers are related to n_ξ and n_η by

$$n = n_\xi + n_\eta + m + 1, \quad l = n_\eta + m, \tag{C36}$$

and are determined by $\rho_\nu(\omega)$ and $\lambda_\nu(\omega)$ in the limit $\omega \to 0$,

$$\rho_\nu(\omega) = \frac{\sqrt{-2\omega}n}{Z_1+Z_2} + O(\omega^{3/2}), \quad \lambda_\nu(\omega) = l(l+1) + O(\omega). \tag{C37}$$

There are 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 $\nu = (n,l,m)$ in the limit $\omega \to 0$:

$$\rho_\nu^T(\omega) = \frac{i\sqrt{2\omega}n}{Z_1+Z_2} + O(\omega^{3/2}), \quad \lambda_\nu^T(\omega) = l(l+1) + O(\omega). \tag{C38}$$

The quasiradial equation (C32) 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 functions are defined only for $\omega > 0$ and $\rho_\nu^S(0) \neq 0$. In the case $Z_1 = Z_2$ the solutions of Eq. (C33) are generalized Legengre 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

$$\rho_\nu^S(0) \approx \frac{(l+1/2)^2}{Z_1+Z_2}\exp\left[\frac{i\pi(2\kappa+m+1)}{2l+1}\right] - \frac{1}{2}. \tag{C39}$$

From Eq. (C39) we see that $\kappa_m < \frac{1}{2}(l-m-1/2)$. In the classification of S Sturmian functions we will use the quantum numbers l, m, and $n = l + \kappa + 1$. Then the set of S-type Sturmian functions is $2p\sigma$, $3d\sigma$, $3d\pi$, $4f\sigma$, $4f\pi$, $4f\delta$, $5f\sigma$, $5g\sigma$, $5g\pi$, $5g\delta, \ldots$.

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

$$\rho_\nu(\omega) = -\frac{\omega}{2(Z_1+Z_2)} + \frac{1}{Z_1+Z_2}\left(\frac{\omega}{2}\right)^{1/2} \times [2n'_\eta + 1 + i\sqrt{2}(2n'_\xi + m + 1)] + O(1),$$
$$\lambda_\nu(\omega) = -\frac{\omega}{2} + \left(\frac{\omega}{2}\right)^{1/2}(2n'_\eta + 1) + O(1), \tag{C40}$$

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

$$n'_\xi = n_\xi + \mathrm{Int}[\tfrac{1}{2}(l-m-\tfrac{1}{2})], \quad n'_\eta = n_\eta, \tag{C41}$$

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.

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

$$C_\nu^S(\omega) = \sqrt{2\pi}\,\exp\left[\sigma_\nu(\omega) - \sigma_\nu(\omega)\ln\left(\frac{i\sigma_\nu(\omega)}{2\sqrt{2\omega}}\right)\right] + O(\omega^{1/2}), \tag{C42}$$

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

At large positive ω the normalization factors $C_\nu(\omega)$ asymptotically behave as

$$C_\nu(\omega) \sim \omega^{n_\xi+(m+1)/2}. \tag{C43}$$

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.

[1] D. R. Bates and R. McCarroll, Proc. R. Soc. London, Ser. A **245**, 175 (1958).

[2] S. B. Schneiderman and A. Russek, Phys. Rev. **181**, A311 (1969).

[3] J. B. Delos, Rev. Mod. Phys. **53**, 287 (1981).

[4] J. Vaaben and K. Taulbjerg, J. Phys. B **15**, 1815 (1981).

[5] E. A. Solov'ev and S. I. Vinitsky, J. Phys. B **18**, L557 (1985).

[6] S. Yu. Ovchinnikov and J. H. Macek, Phys. Rev. A **55**, 3605 (1997).

[7] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **70**, 872 (1976) [Sov. Phys. JETP **43**, 453 (1976)].

[8] S. Ovchinnikov and J. Macek, Phys. Rev. Lett. **75**, 2474 (1995).

[9] See, e.g., M. Rakovic and E. A. Solov'ev, Phys. Rev. A **41**, 3635 (1990).

[10] R. McCarroll and D. S. F. Crothers, Adv. At. Mol. Opt. Phys. **32**, 253 (1994).

[11] T. P. Grozdanov and E. A. Solov'ev, Phys. Rev. **42**, 2703 (1990); **44**, 5605 (1991).

[12] E. A. Solov'ev, Teor. Mat. Fiz. **28**, 240 (1976) [Theor. Math. Phys. **28**, 757 (1976)].

[13] E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Collisions* (Springer-Verlag, New York, 1984), p. 57ff.

[14] See, e.g., E. A. Solov'ev, Usp. Fiz. Nauk **157**, 437 (1989) [Sov. Phys. Usp. **32**, 228 (1989)].

[15] D. B. Khrebtukov and J. H. Macek, J. Phys. A (to be published).

[16] P. A. Braun, Rev. Mod. Phys. **65**, 115 (1993).

[17] B. Piraux and R. Shakeshaft, Phys. Rev. A **49**, 3903 (1994).

[18] D. I. Abramov, S. Yu. Ovchinnikov, and E. A. Solov'ev, Phys. Rev. A **42**, 6366 (1990).

[19] M. Pieksma, S. Y. Ovchinnikov, J. van Eck, W. B. Westerveld, and A. Niehaus, Phys. Rev. Lett. **73**, 46 (1994).

[20] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **81**, 1681 (1981) [Sov. Phys. JETP **54**, 893 (1981)].

[21] M. Pieksma and S. Y. Ovchinnikov, J. Phys. B **24**, 2699 (1991).

[22] E. A. Solov'ev, Phys. Rev. A **42**, 1331 (1990).

[23] M. Pieksma and S. Y. Ovchinnikov, J. Phys. B **27**, 4573 (1994).

[24] J. Macek and S. Ovchinnikov, Phys. Rev. A **54**, 544 (1997).

[25] Yu. N. Demkov, in *Invited Papers of the Fifth International Conference on the Physics of Electronics and Atomic Collisions, Leningrad, 1967*, edited by L. Branscomb (University of Colorado, Boulder, 1968), p. 186.

[26] M. Pieksma and S. Y. Ovchinnikov, Comments At. Mol. Phys. **31**, 21 (1995).

[27] R. Shakeshaft, J. Phys. B **18**, L611 (1985); Phys. Rev. A **34**, 244 (1986); **34**, 5119 (1986).

[28] I. V. Komarov, L. I. Ponomarev, and S. Y. Slavyanov, *Spheroidal and Coulomb Spheroidal Functions* (Nauka, Moscow, 1976), p. 24.