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TWO-DIMENSIONAL RESONANCES IN COULOMB FEW BODY SYSTEM AND THEORY OF ELECTRON ENERGY AND ANGULAR DISTRIBUTION

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ABSTRACT

The two-dimensional resonances in the problem of two Coulomb centers are discussed. The *ab initio* calculation of electron energy and angular distributions of saddle-point and S-promotion electrons for ionization in proton-hydrogen atom collisions are presented. The calculation is based on an outgoing wave Sturmian expansion in the frequency domain. It goes beyond the usual Born-Oppenheimer separation of electron and nuclei motions and displays the "$v/2$" peak and the continuum cusp, missing in previous theories.

1. Introduction

In an exact numerical calculation of the S-matrix poles of the problem of two Coulomb centers Ovchinnikov and Solov'ev[1] discovered new quasistationary states with a small width, whose origin was unclear since they could not be related to any features in the behavior of the effective potential. Later they[2] showed that, despite the exact separation of variables in the Schrodinger equation, these narrow resonances cannot be explained in terms of the quasi-radial one-dimensional problem exclusively, and therefore the multidimensional nature of the system plays a key role. The effective potential of the quasi-radial equation after separation of variables in spheroidal coordinates has the same form as the radial potential of the hydrogen atom for which there are no known quasistationary states. Nevertheless quasistationary states appear. This is completely due to the energy dependence of the separation constant (this energy dependence naturally arises from the quasi-angular equation), which reflects the multidimensionality of the problem.

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The resonances are associated with capture of classical particles by unstable equilibrium states. In this case scattering occurs in such a way that paths of particles approach the internuclear axis asymptotically and reach this axis in the limit $t \to \infty$ after an infinite number of oscillations. Such paths, resulting in capture of particles have been discussed for the problem of two centers in celestial mechanics back in the last century.

From the point of view of ionization these quasistationary states are related to the S-promotion of diabatic states to the continuous spectrum. In order to calculate total ionization cross sections it is sufficient to know the characteristics of these quasistationary states. The problem of calculating the spectrum, which we shall consider below, is more complicated.

Present theories usually cannot calculate energy and angular distributions of electrons and especially cannot get the continuum capture cusp which should be present in the spectra. Previous calculations of total cross sections have identified two ionization mechanisms[4,5] at low-energy collisions, called T-promotion and S-promotion, but have not been able 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 of the collision system in between the nuclei. For equal charges, their velocities k will be distributed around one-half of the velocity of the incoming particles. Recent calculations[6,7] obtain such a distribution for saddle-point electrons, but employ an adjustable parameter R_{ion}, where adiabatic and diabatic approaches are matched. One objective of the present calculations is to 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. 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 theory cannot compute the complete distribution of these electrons. We will show that the S-mechanism is the responsible for the continuum capture cusp, missing in previous theories.

2. Outgoing wave Sturmian expantions and coupled equation in the frequency domain

We consider the time-dependent Schrödinger equation used in the theory of ion-

atom collisions

$$\left[i\frac{\partial}{\partial t} - H(R(t),\mathrm{r})\right]\psi(t,\mathrm{r}) = 0. \tag{1}$$

Following Solov'ev[8] we introduce scaled variables $\mathrm{q} = \mathrm{r}/R$. In addition to this change of variables, the wave function ψ is transformed according to

$$\psi(t,\mathrm{r}) = R^{-3/2}\exp\left[i\frac{1}{2}\frac{\dot{R}}{R}q^2\right]\psi(\tau,\mathrm{q}) \tag{2}$$

and a new time variable $d\tau = dt/R^2(t)$ is introduced. Then the time-dependent Schrödinger equation in the case of straight-line motion of nuclei becomes

$$\left[i\frac{\partial}{\partial\tau} - H_0(\mathrm{q}) + R(\tau)V(\mathrm{q})\right]\psi(\tau,\mathrm{q}) = 0\,, \tag{3}$$

where

$$H_0(\mathrm{q}) = -\frac{1}{2}\nabla_{\mathrm{q}}^2 + bv\ell_x + \frac{(bv)^2}{2}q^2,$$

$$V(\mathrm{q}) = \left(-\frac{Z_1}{|\mathrm{q}-\hat{\mathrm{R}}/2|} - \frac{Z_2}{|\mathrm{q}+\hat{\mathrm{R}}/2|}\right),$$

$$R(\tau) = -\frac{b}{\sin(vb\tau)} \tag{4}$$

and where b is the impact parameter, v is the incident velocity, ℓ_x is the projection of the angular momentum operator for the electron on the axis perpendicular to the scattering plane, and Z_1 and Z_2 are the charges of the two nuclei[8]. Note that this equation contains an extra potential term $(bvq)^2/2$, which arises from the transformation to scaled coordinates.

In standard theories $\psi(\tau,\mathrm{q})$ is expanded in fixed-nucleus basis states, i.e. eigenstates of $H_0 + RV$. These states cannot represent the ionization spectrum correctly and the continuum capture cusp is always absent in standard fixed-nucleus calculations. To incorporate dynamic variations of $R(\tau)$ we write the wavefunction as the Fourier transform (Solov'ev[9] used the Laplace transformation in r-space),

$$\psi(\tau,\mathrm{q}) = (2\pi vi)^{-1/2}\int_{-\infty}^{\infty} d\omega\exp(-i\omega\tau)\tilde{\psi}(\omega,\mathrm{q}) \tag{5}$$

and consider the Schrödinger equation in the frequency domain ω. In the frequency domain the wavefunction $\tilde{\psi}_i(\omega,\mathrm{q})$ that corresponds to the initial bound state is expanded in terms of eigenfunctions with fixed ω, i.e. Sturmian eigenfunctions:

$$\tilde{\psi}_i(\omega,\mathrm{q}) = \sum_n \phi_n(\omega,\mathrm{q})B_n^i(\omega)\,, \tag{6}$$

where the Sturmian basis set $\{\phi_n\}$ is defined by

$$[H_0(\mathbf{q}) + R_n(\omega)V(\mathbf{q})]\phi_n(\omega,\mathbf{q}) = \omega\phi_n(\omega,\mathbf{q}) \tag{7}$$

with outgoing wave boundary conditions at $\omega > 0$

$$\frac{\frac{\partial\phi_n(\omega)}{\partial q}}{\phi_n(\omega)} \longrightarrow ip, \quad \text{as } q \longrightarrow \infty,$$

where $p\sqrt{2\omega}$. In Eq.(7) $R_n(\omega)$ are the Sturmian eigenvalues and $\phi_n(\omega,\mathbf{q})$ are Sturmian eigenfunctions. normalized according to

$$< \phi_n(\omega)|V|\phi_{n'}(\omega) >= \delta_{nn'} \, . \tag{8}$$

The wavefunction $\tilde{\psi}_{\mathbf{k}}(\omega,\mathbf{q})$ that corresponds to the initial continuum state cannot be completely represented by outgoing wave Sturmians. The incoming part of the wavefunction should be added explicitly:

$$(2\pi)^{3/2}\tilde{\psi}_{\mathbf{k}}(\omega,\mathbf{q}) = \frac{\exp\left(-ip|\mathbf{q}+\frac{\mathbf{k}}{v}|\right)}{|\mathbf{q}+\frac{\mathbf{k}}{v}|} + \sum_n \phi_n(\omega,\mathbf{q})B_n^{\mathbf{k}}(\omega) \, . \tag{9}$$

There are some exactly solvable problems where one Sturmian gives the exact solution (e.g., if V is a projection operator[10] or two zero-range potentials[11]). Thus we have the remarkable result that while the set of Sturmians is not complete in that it may have only one member for a fixed ω, it is nonetheless complete enough to solve the original time-dependent Schrödinger equation.

To illustrate the approach, consider the case with $b = 0$,i.e. $R = vt = -1/v\tau$. By the usual manipulations, one obtains for the expansion coefficients

$$B_n^{\mathbf{i}}(\omega) = \frac{A_n^{\mathbf{i}}(\omega)}{R_n(\omega)}\exp\left[\frac{i}{v}\int_0^\omega \frac{d\omega'}{R_n(\omega')}\right] \quad \text{and} \quad B_n^{\mathbf{k}}(\omega) = \frac{A_n^{\mathbf{k}}(\omega)}{R_n(\omega)}\exp\left[\frac{i}{v}\int_0^\omega \frac{d\omega'}{R_n(\omega')}\right]$$

a set of coupled equations

$$\frac{\partial A_n^{\mathbf{i}}(\omega)}{\partial\omega} + \sum_{n'} \frac{< \phi_n(\omega)|\phi_{n'}(\omega) >}{R_n(\omega) - R_{n'}(\omega)}\exp\left\{\frac{i}{v}\int_0^\omega d\omega'\left[\frac{1}{R_{n'}(\omega')} - \frac{1}{R_n(\omega')}\right]\right\} A_{n'}^{\mathbf{i}}(\omega) = 0 \tag{10}$$

and

$$\frac{\partial A_n^{\mathbf{k}}(\omega)}{\partial\omega} + \sum_{n'} \frac{< \phi_n(\omega)|\phi_{n'}(\omega) >}{R_n(\omega) - R_{n'}(\omega)}\exp\left\{\frac{i}{v}\int_0^\omega d\omega'\left[\frac{1}{R_{n'}(\omega')} - \frac{1}{R_n(\omega')}\right]\right\} A_{n'}^{\mathbf{k}}(\omega) =$$
$$i\frac{2\pi}{vR_n(\omega)}\exp\left[-\frac{i}{v}\int_0^\omega \frac{d\omega'}{R_n(\omega')}\right]\phi_n\left(\omega,\frac{\mathbf{k}}{v}\right) \tag{11}$$

with initial conditions

$$A_n^i(-\infty) = \delta_{in} \quad \text{and} \quad A_n^k(-\infty) = 0\,.$$

There are two different subsets of Sturmians related to S and T promotions. The Sturmians associated with the S-promotion are defined only for $\omega > 0$ and $R_n^S(0) \neq 0$. In contrast the T-promotion Sturmians exist for all ω and $R_n^T(0) = 0$. The coupling terms between n and $n' = n+1$ in Eqs.(10) and (11) have pole singularities at $\omega = 0$. All other coupling terms are small. The coefficient $A_{n'}(\omega)$ and $A_{n'}^k(\omega)$ are obtained by solving Eqs.(10) and (11) using a transformation that remove the singularities in the coupled equations. The resulting equations are solved in a one channel approximation.

3. Differential ionization probabilities

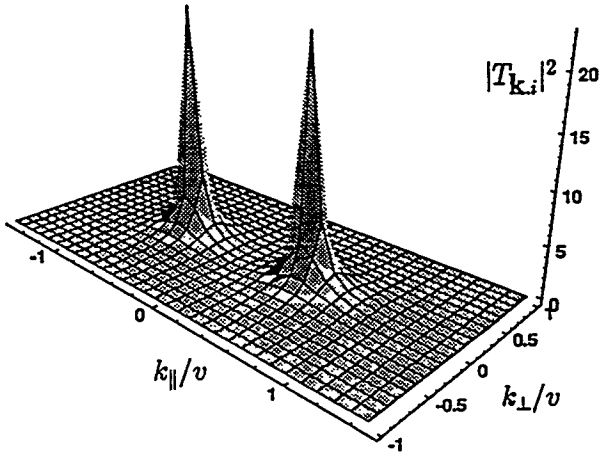

Figure 1. The differential ionization probabilities $|T_{k,i}|^2$ at $v = 0.4$ a.u. for S-promotion.

The transition amplitude to the continuum is given by the matrix elements[11]

$$T_{k,i} = < \psi_k^{out}(t) | \psi_i^{in}(t) > \ . \tag{12}$$

Using the fact that the transition amplitude does not depend on the time and the Sturmian eigenstates may be written in the form (see Eq.(4.10) in Ref.[4])

$$\phi_n(\omega, \mathbf{q}) = C_n(\omega)\chi_n(\omega, \mathbf{q}) \tag{13}$$

where $\chi_n(\omega, \mathbf{q})$ is a wavefunction normalized to the δ function on the energy scale ω and $C_n(\omega)$ is a normalization constant, we obtain

$$T_{k,i} = \frac{1}{\pi v} \sum_n \int_0^\infty d\omega \frac{C_n(\omega) A_n^i(\omega)}{R_n(\omega)} \exp\left[\frac{i}{v}\int_0^\omega \frac{d\omega'}{R_n(\omega')}\right]$$

$$\Im\left\{\frac{C_n(\omega)A_n^{\mathbf{k}}(\omega)}{R_n(\omega)}\exp\left[\frac{i}{v}\int_0^{\omega}\frac{d\omega'}{R_n(\omega')}\right]\right\}. \qquad (14)$$

Two spectra of ejected electrons associated with two different kinds of Sturmians are displayed in Fig. 1 and Fig. 2. 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. The energy distribution of the fast electrons is exponential.

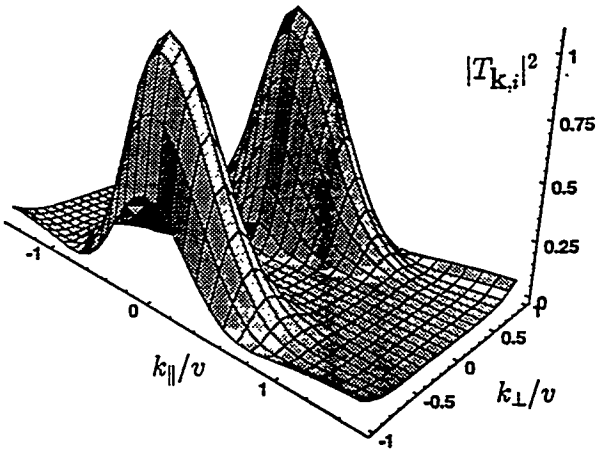

Figure 2. The differential ionization probabilities $|T_{\mathbf{k},i}|^2$ at $v = 0.4$ a.u. for T-promotion.

Figure 2 shows a spectrum related to the T-promotion of the $2p\pi$-state for $v = 0.4$ a.u. The two peaks at zero center-of-mass velocity are associated with the π-symmetry of the T_{01}-promotion.

4. Conclusions

Our formulation in terms of outgoing wave Sturmian eigenfunctions present a complete *ab initio* theory of ionization in low energy ion-atom collisions. First calculations show that the 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 arbitary adjustable parameters. The S-promotion mechanism gives rise to two cusps where electron velocities match the ion velocities. These calculations show how measured electron distributions may be interpreted in terms of identifiable physical mechanisms, using our new representation Eq.(9). If measurements of the electron energy and angular distributions of emitted electrons could be performed for small impact parameters b, than these calculations for $b = 0$ can quantitatively be

compared with spectra presented at Fig. 1. However, measurements integrated over the impact parameter should still show the feature described here.

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