Chapter 12
Potential Splitting Approach for Atomic and Molecular Systems

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Abstract In order to describe few-body scattering in the case of the Coulomb interaction, an approach based on splitting the reaction potential into a finite range part and a long range tail part is presented. The resulting driven Schrödinger equation with asymptotic outgoing waves is solved with the exterior complex scaling. The approach is illustrated with calculations of the electron scattering on the hydrogen atom and the positive helium ion. The scattering processes in the $H^+ - H_2^+$ system with one-state electronic energy surface have also been studied.

12.1 Introduction

Systems with Coulomb interactions are often considered in nuclear, atomic, and molecular physics. Scattering problems for them are of great interest for many physical processes. The complicated boundary conditions at large distances are a major difficulty for these problems [1]. Several methods have been developed for constructing solutions to the three-body scattering problem [2]. Some of them avoid using the explicit asymptotic form of the wave function.

In several recent studies, we have reported a method which is capable to correctly treat the Coulomb scattering problem using exterior complex scaling (ECS) [3–6]. The key point of this method is splitting the long-range Coulomb potential into the core and tail parts. The tail part is used to construct the distorted incident wave, which is responsible for the asymptotic Coulomb dynamics. The core part of the potential generates an inhomogeneous term in the Schrödinger equation making possible the application of ECS for solving the equation. Here we outline the potential splitting approach and present its application to study atomic systems and molecular systems with *ab initio* potentials.

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12.2 Theoretical Approach

The three-body quantum system is described with the Schrödinger equation in Jacobi coordinates $\mathbf{x}_\alpha, \mathbf{y}_\alpha$ with the Hamiltonian

$$H = T_{\mathbf{x}_\alpha} + T_{\mathbf{y}_\alpha} + V(\mathbf{x}_\alpha, \mathbf{y}_\alpha),$$

where $T_{\mathbf{x}_\alpha}$, $T_{\mathbf{y}_\alpha}$ are the kinetic energy operators, and $V(\mathbf{x}_\alpha, \mathbf{y}_\alpha)$ is the full interaction in the system. The total wave function Ψ of the system is written as the sum $\Psi = \Phi + \Psi^R$, and the function Φ satisfies the driven equation

$$(H - E)\,\Phi = -V_R \Psi^R. \tag{12.1}$$

Here the distorted incident wave $\Psi^R(\mathbf{x}_\alpha, \mathbf{y}_\alpha)$ is introduced as a solution to the scattering problem with the sum of the potential in the target pair $V_\alpha(\mathbf{x}_\alpha)$ and the tail potential $V^R(\mathbf{x}_\alpha, \mathbf{y}_\alpha)$. The full potential is split into the sum of $V_\alpha(\mathbf{x}_\alpha)$, the core $V_R(\mathbf{x}_\alpha, \mathbf{y}_\alpha)$ and the tail V^R parts: $V(\mathbf{x}_\alpha, \mathbf{y}_\alpha) = V_\alpha(\mathbf{x}_\alpha) + V_R + V^R$. Here $V_R = V - V_\alpha$ for $y_\alpha \le R$, and $V_R = 0$ for $y_\alpha > R$. Details of the splitting procedure is described in the papers [5, 6]. The right hand side of equation (12.1) is of finite range with respect to the variable y_α. Thus this equation can be solved numerically with the ECS transformation [7].

In order to find scattering amplitudes and cross sections, the asymptotic form of the scattered wave function at large distances is used [1]. Projecting the asymptotic representation on the two body wave functions, the local representation for the partial amplitude can be derived [6].

12.3 Applications of the Potential Splitting Method

12.3.1 Atomic Systems

First, our approach is applied to the scattering problem in the electron-H and electron-He$^+$ systems. These systems are of fundamental importance in atomic physics and have been studied by various methods and approximations, see [8] and references therein. The numerical solution of the driven equation (12.1) is performed with the finite element method, which is described in details in [9]. The grid used in our calculations is given in [6].

Our results for the singlet 1s→ns cross sections for the e-H and e-He$^+$ scattering are presented in Fig. 12.1. In both cases the calculated cross sections display complicated resonance behaviour. The resonance structure of the e-He$^+$ cross section occur at lower energies due to the presence of the asymptotic Coulomb interaction. The comparison of our data with other theoretical results [8, 10] shows the relative difference less than 10^{-3}.

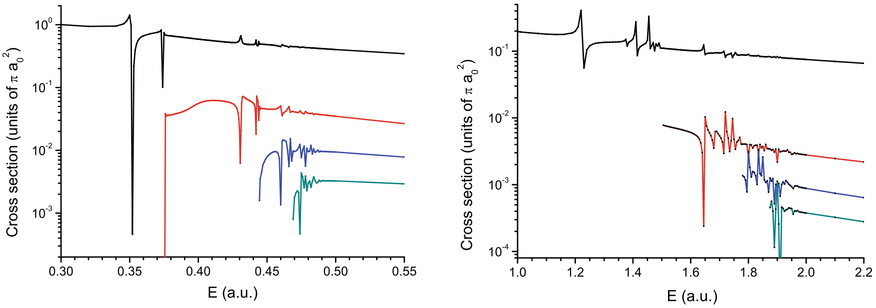

Fig. 12.1 The singlet (spin weight included) 1s→1s, 2s, 3s, 4s cross sections (from above) for the e-H (left) and e-He$^+$ (right) scattering as functions of the electron energy, Adapted from [6]

12.3.2 Molecular Systems

Molecular systems cannot be exactly studied with few-body analytical methods as the total number of particles is too large. To apply such methods, additional approximations are necessary. The most obvious one is the Born-Oppenheimer approximation where the electron degrees of freedom do not participate in the dynamical equations but are averaged to the potential energy surfaces. For accurate calculation of processes, numerical *ab-initio* potentials calculated with quantum chemistry approaches must be used. These potentials depend on all internuclear distances, and are given numerically. The ECS approach can be used to calculate scattering processes with this type of potentials provided that the scaling radius is larger than the internuclear distance where the potential is numerically calculated. For systems with asymptotic Coulomb interactions, the potential splitting approach has been used.

In this work, we have considered the H$^+$ – H$_2^+$ scattering. The potential energy surface $U(r_1, r_2, \theta)$ of the electronic ground state of H$_3^{2+}$ depends on the two bond-lengths r_1, r_2, and the angle θ between them. The potential is computed using the aug-cc-pVQZ basis set of Dunning [11]. The *ab initio* calculations are carried out using internal coordinates where the bond-lengths are varied in the range $0.8a_0 \leq r_i \leq 20.0a_0$, and the angle θ is varied in $[0, \pi]$. These calculations have been performed with the MOLPRO program [12]. For the regions where two nuclei come close together and the asymptotic regions at large internuclear distances, the *ab initio* potential energy surface is extrapolating and interpolated by first introducing the function

$$U(r_1, r_2, \theta) = V(r_1, r_2, \theta) - \sum_{i=1}^{3} E_{H_2^+}(r_i). \qquad (12.2)$$

where r_3 is calculated as $r_3 = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}$. The energy $E_{H_2^+}(r)$ is the energy of the Coulomb two-centre problem with the electron and two charges +1

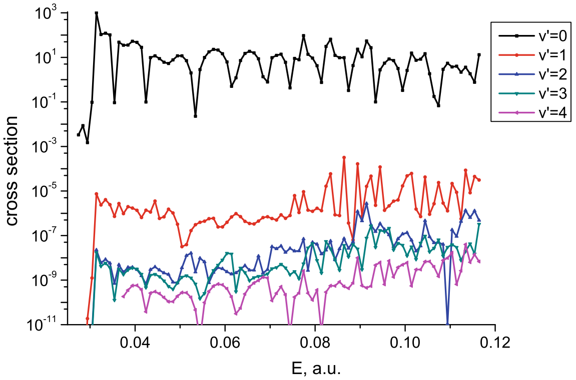

Fig. 12.2 The elastic and excitation cross sections for the $H^+ - H_2^+$ scattering

each placed at the distance r. The function $U(r_1, r_2, \theta)$ has no singularities at $r_i = 0$ and hence is much easier to interpolate and extrapolate.

Using the united atom approximations, we can find the values of U when the distances between two or three protons approach zero. For bond-lengths in the range $r_i \leq 20.0a_0$, the potential energy surface is calculated at an arbitrary point with the 3D spline interpolation.

As we use the ECS, the potential energy must be represented by an analytical function at large distances. In order to make this representation, we use a combination of the asymptotic Coulomb potential and the polarization potential $1/r_i^2$. The coefficients are chosen to make the total potential energy continuous on the boundary of the numerical grid.

We have calculated the elastic and excitation scattering cross sections $H_2^+(v = 0, J = 0) + H^+ \to H_2^+(v', J' = 0) + H^+$ with the constructed potential energy surface. In the calculations, we use a rectangular product grid. For the reaction coordinate y_α, five finite elements have been used at short distance [0–4] a.u., 44 elements for intermediate region, and ten elements of total length 40 a.u. for the discretization beyond the splitting point $R = 31$ a.u. For the coordinate x_α, 19, 9, and 4 elements respectively have been used for the regions mentioned above. One element has been used for the angular variable θ_α.

Our results for the elastic and excitation $H_2^+(v = 0, J = 0) \to H_2^+(v', J' = 0)$ cross sections for the $H^+ - H_2^+$ scattering are presented in Fig. 12.2, where the energy E is the incident energy of H^+. The structure in the cross section appears because of large number of states in the H_2^+ molecule.

12.4 Conclusions

We have proposed the mathematically sound approach for calculations of scattering processes. The potential splitting approach allows for the solution of the scattering problem with the Coulomb interaction. Besides systems with analytically given interactions, molecular systems with numerically defined *ab initio* potentials can be studied with the combined ECS and splitting potential approaches.

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