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Matrix elements of the transition operator evaluated off the energy shell: Analytic results for the hard-core plus square-well spherical potential

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An analytic expression is presented for the off-shell T-matrix elements for scattering from the spherical hard-core plus square-well potential. Various analytical properties of the off-shell T matrix, such as symmetry and unitarity, are examined. The typical behavior of the off-shell T matrix is shown numerically. It is found that the behavior strongly depends on the three independent quantities, i.e., the energy and the initial and final momenta, which can be off the energy shell. These results, combined with multiple-scattering theory, can be used to study high-energy many-body collision processes, such as collision-induced dissociation.

I. INTRODUCTION

Rigorous quantum-mechanical treatments of molecular collisions rely on expanding the scattering wave function in a set of basis functions, usually chosen to be the eigenstates of the noninteracting collision partners. Unfortunately, such expansions become computationally unfeasible for polyatomic systems due to the large number of eigenstates that must be included in calculations. This is particularly the case for scattering from solids containing defects and/or adsorbates that break the periodicity of the surface, and thus lead to continuous sets of basis functions. The situation is more complicated (even in the gas phase) when one attempts to describe atomic rearrangements, i.e., reactive collisions, since the basis sets appropriate to initial- and final-arrangement channels are usually incompatible with each other.

An alternative quantal approach, namely multiple-scattering theory,[1] first postulates that the overall potential can be expressed in terms of sums of interactions between pairs of atoms, and then decomposes the transition operator into sums of sequences of successive collisions, each of which involves only two atoms. Basis-set expansions can thus be avoided to a large degree, so that multiple scattering in principle seems to be a very promising approach to describing energy transfer[2] and rearrangements[3] in polyatomic systems. Accordingly, we have begun a systematic application of multiple-scattering theory to gas-solid collisions involving nonperiodic surfaces as well as rearrangements,[4] of which the present article describes one of its fundamental components. In particular, multiple-scattering calculations require knowledge of matrix elements of two-atom transition operators T with respect to momentum eigenstates $|\mathbf{p}\rangle$ and $|\mathbf{p}'\rangle$ that are said to be off the energy shell, i.e., $\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$ for $p'^2/(2m)\neq p^2/(2m)\neq E$. The need for such quantities becomes evident when one considers that the two-atom interactions are intermediate events that do not necessarily correspond to the initial and final relative momenta of the (composite) collision partners. More specifically, whenever $\mathbf{p}$ and/or $\mathbf{p}'$ do not correspond to the total energy E, then the resulting $\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$ may be interpreted as the contribution due to an "incomplete" two-atom collision,[5] i.e., an intermediate event for which the initial and/or final separation remains finite. This article considers the evaluation of off-shell T-matrix elements for model two-atom potentials to be used in subsequent studies of gas-surface collisions.[4]

Fully off-shell T-matrix elements are available in analytic form only for simple potentials (i.e., hard core and Coulomb[6]). Unfortunately, at present there is no efficient and accurate method to calculate the full off-shell T matrix for more sophisticated potentials, because one must first solve the off-shell analog of the Lippmann-Schwinger equation for each partial wave. Consequently, most numerical treatments have been restricted to the case of very low angular momenta;[7,8] however, the contributions from large angular momenta are more important to atomic and molecular scattering at superthermal impact energies. Attempts have been made with various approximations to get some insight into the behavior of the two-body off-shell T matrix. For example, Van Leeuwen and Reiner[9] proposed to model the potential in terms of a sequence of step functions. Alternatively, Korsch[10,11] and Gerber[3] have developed semiclassical approximations for specific ranges of the momenta. However, several classes of many-body collisions require knowledge of the fully off-shell T matrix over the entire momentum space.[4]

A computationally practical expression for the off-shell T matrix of a reasonable atom-atom potential would be very useful to systematically apply multiple-scattering theory to many-atom collision processes, and particularly to collision-induced dissociation. Accordingly, we have derived the exact expression for the fully off-shell T matrix of a model potential that includes the most important features of typical atomic interactions: steeply repulsive forces at small distances, which we presently model by a hard core, plus an attractive well at intermediate distances, which we represent by a square well. In spite of its obvious simplicity, the hard-core plus square-well model is expected to give at least a qualitative representation of typical off-shell T matrices, provided that the energy is much larger than the well depth, since in those cases collisions are mostly governed by the repulsive short-range forces. Furthermore, the addition of the square well is intended to mimic the role of the binding forces prior to dissociation. The present model is thus consistent with its intended use in multiple-scattering treatments that are appropriate to high impact energies.[4] In addition, one expects that the exact solution for the present potential will provide some basic information about the qualitative behavior of fully off-shell T matrices with respect to changes in the momenta, scattering angle, and energy, as well as serve as a reference when developing approximations to off-shell T matrices for more realistic potentials.

The present work is organized as follows. In Sec. II we outline the algebraic procedure leading to the off-shell T matrix for the model potential. Van Leeuwen and Reiner[9] briefly considered the present potential as a limiting case of piecewise-constant potentials. They thus arrived at an expression for the T matrix that is computationally impractical since it requires the evaluation of the determinant of a large matrix for each partial wave. Moreover, the evaluation of such determinants would be numerically unstable since their elements have widely differing magnitudes. Instead, we have taken an independent approach that directly expresses the off-shell T matrix in terms of Ricatti-Bessel functions (without need of inverting matrices), and thus allows one to devise a stable computational procedure. We also verify that these results satisfy unitarity and symmetry upon exchange of momentum variables. Next, Sec. III outlines the computational procedure for the present potential, which efficiently calculates the large numbers of partial waves (e.g., $l \sim 1000$) usually required for superthermal collisions. Section IV then presents calculations to illustrate the behavior of the fully off-shell T matrix with respect to changes in the momenta, scattering angle, energy, and parameters of the potential. Finally, Sec. V summarizes the conclusions derived from this work.

II. THE OFF-SHELL T MATRIX AND ITS PROPERTIES

In order to obtain the fully off-shell T matrix, one first considers the following operator equation, which is equivalent to the Lippmann-Schwinger equation,[12] for the Møller wave operator Ω,

$$(E-H)\Omega(E^+)=E-H_0\ , \tag{1}$$

where H_0 is the kinetic-energy operator, $H=H_0+V$, and V is the potential. Next, one takes matrix elements of both sides of the equation with respect to $\langle \mathbf{r}|$ and $|\mathbf{p}\rangle$, where $\mathbf{p}$ can be off the energy shell. Noting that $\Psi_{\mathbf{p}}(\mathbf{r};E^+)=\langle \mathbf{r}|\Omega(E^+)|\mathbf{p}\rangle$, one arrives at the differential equation for the off-shell wave function $\Psi_{\mathbf{p}}(\mathbf{r};E^+)$,

$$\left[E+\frac{\hbar}{2\mu}\nabla^2-V(\mathbf{r})\right]\Psi_{\mathbf{p}}(\mathbf{r};E^+) =(2\pi\hbar)^{-2/3}\left[E-\frac{p^2}{2\mu}\right]e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\ . \tag{2}$$

The energy E here plays the role of a parameter that need not be equal to the total energy of the system, since off-shell T matrices are ultimately used in many-body formalisms of the Faddeev type.[1] Since we are presently considering spherically symmetric potentials, we expand $\Psi_{\mathbf{p}}(\mathbf{r};E^+)$ in the conventional partial wave form

$$\Psi_{\mathbf{p}}(\mathbf{r};E^+)=(8\pi^3\hbar)^{-1/2}\frac{1}{pr}\times\sum_{l=0}^{\infty}(2l+1)i^lP_l(\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})\omega_l(r,p;E^+)\ , \tag{3}$$

where $\mathbf{p}$ indicates the initial momentum, while $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ denote unit vectors in the directions of $\mathbf{p}$ and $\mathbf{r}$, respectively. Hence the radial off-shell wave function $\omega_l(r,p;E^+)$ satisfies the inhomogeneous equation

$$\left[\frac{d^2}{dr^2}+\frac{2\mu}{\hbar^2}[E-V(r)]-\frac{l(l+1)}{r^2}\right]\omega_l(r,p;E^+) =\frac{(p_E^2-p^2)}{\hbar^2}\hat{j}_l\left[\frac{pr}{\hbar}\right]\ , \tag{4}$$

where $\hat{j}_l$ is the Riccati-Bessel function.

In this article, we take the potential V to be the hard-core plus square-well potential defined by

$$V(r)=\begin{cases}\infty, & r\le a\\ -V_0, & a<r<b\\ 0, & r\ge b\ .\end{cases} \tag{5}$$

Upon taking into account the boundary condition for the radial equation[10] as well as the continuity of $\omega_l(r,p;E^+)$ and of its first derivative at $r=a$ and b, after much algebra one arrives at the following expression for $\omega_l(r,p;E^+)$:

$$\omega_l(r,p;E^+)=\begin{cases}0, & r\le a\\ \alpha_l\hat{j}_l\left[\frac{qr}{\hbar}\right]+\beta_l\hat{h}_l^{(1)}\left[\frac{qr}{\hbar}\right]+\frac{p_E^2-p^2}{q^2-p^2}\hat{j}_l\left[\frac{pr}{\hbar}\right], & a<r<b\\ \hat{j}_l\left[\frac{pr}{\hbar}\right]+\gamma_l\hat{h}_l^{(1)}\left[\frac{p_Er}{\hbar}\right], & r\ge b\ ,\end{cases} \tag{6}$$

with

$$q=(p_E^2+2\mu V_0)^{1/2},\quad p_E=\sqrt{2\mu E}\ , \tag{7}$$

and

$$\alpha_l = \left\{ (q^2-p_E^2)\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\left[p_E\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]\hat{j}_l\left[\frac{pb}{\hbar}\right]-p\hat{j}_{l-1}\left[\frac{pb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]\right] + (p_E^2-p^2)\hat{j}_l\left[\frac{pa}{\hbar}\right]\left[p_E\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]-q\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]\right]\right\}\Big/ D_l , \tag{8a}$$

$$\beta_l = \left\{ (q^2-p_E^2)\hat{j}_l\left[\frac{qa}{\hbar}\right]\left[p\hat{j}_{l-1}\left[\frac{pb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]-p_E\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]\hat{j}_l\left[\frac{pb}{\hbar}\right]\right] + (p_E^2-p^2)\hat{j}_l\left[\frac{pa}{\hbar}\right]\left[q\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]-p_E\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]\hat{j}_l\left[\frac{qb}{\hbar}\right]\right]\right\}\Big/ D_l , \tag{8b}$$

$$\gamma_l = \left[(q^2-p_E^2)\left\{ q\hat{j}_l\left[\frac{pb}{\hbar}\right]\left[\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]-\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{qa}{\hbar}\right]\right] + p\hat{j}_{l-1}\left[\frac{pb}{\hbar}\right]\left[\hat{j}_l\left[\frac{qa}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]-\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{qb}{\hbar}\right]\right]\right\} - iq(p_E^2-p^2)\hat{j}_l\left[\frac{pa}{\hbar}\right]\right]\Big/ D_l , \tag{8c}$$

where

$$D_l = (q^2-p^2)\left\{ q\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]\left[\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{qa}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\right] + p_E\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]\left[\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{qb}{\hbar}\right]-\hat{j}_l\left[\frac{qa}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]\right]\right\} . \tag{9}$$

The wave function $\omega_l(r,p;E^+)$ contains only part of the information about the fully-off-shell T matrix, because it depends on only one momentum variable (i.e., the initial momentum). We will show later how the half-off-shell T matrix is evaluated from the above expression for $\omega_l(r,p;E^+)$. For this purpose one first requires the momentum representation of the off-shell wave function. Utilizing the partial-wave expansion of the plane wave and the orthogonality condition of the Legendre polynomials, the wave function in momentum space can be expressed as

$$\begin{aligned}\Phi_{\mathbf{p}}(\mathbf{p}';E^+) &= \langle \mathbf{p}'|\Omega(E^+)|\mathbf{p}\rangle \\ &= \int \langle \mathbf{p}'|\mathbf{r}\rangle\langle \mathbf{r}|\Omega(E^+)|\mathbf{p}\rangle d\mathbf{r} \\ &= \frac{1}{2\pi^2\hbar pp'}\sum_{l=0}^{\infty}(2l+1)P_l(\hat{\mathbf{p}}'\cdot\hat{\mathbf{p}})\int_0^{\infty}\hat{j}_l\left[\frac{p'r}{\hbar}\right]\omega_l(r,p;E^+)dr\end{aligned} \tag{10}$$

with the normalization

$$\langle \mathbf{p}'|\mathbf{p}\rangle = \delta(\mathbf{p}'-\mathbf{p}) . \tag{11}$$

The integral appearing in Eq. (10) is then evaluated over each of the three subranges specified by Eq. (6). There is no contribution from the range $0<r<a$ where $\omega_l(r,p;E^+)$ is identically zero. It is also straightforward to perform the second integration in the region $a<r<b$, because the integral of two Bessel functions in a finite region has a closed form.[13] The evaluation of the third integral (i.e., over the range $b<r<\infty$) requires the following identities:

$$\int_b^{\infty}\hat{j}_l\left[\frac{p'r}{\hbar}\right]\hat{j}_l\left[\frac{pr}{\hbar}\right]dr = \frac{\pi\hbar}{2}\delta(p'-p)+\frac{\hbar}{p'^2-p^2}\left[p\hat{j}_{l+1}\left[\frac{pb}{\hbar}\right]\hat{j}_l\left[\frac{p'b}{\hbar}\right]-p'\hat{j}_{l+1}\left[\frac{p'b}{\hbar}\right]\hat{j}_l\left[\frac{pb}{\hbar}\right]\right] , \tag{12a}$$

$$\int_b^{\infty}\hat{j}_l\left[\frac{p'r}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{pr}{\hbar}\right]dr = \frac{\pi\hbar}{2}\delta(p'-p)+\frac{\hbar}{p'^2-p^2}\left[p'\hat{j}_{l+1}\left[\frac{p'b}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{pb}{\hbar}\right]-p\hat{h}_{l+1}^{(1)}\left[\frac{pb}{\hbar}\right]\hat{j}_l\left[\frac{p'b}{\hbar}\right]\right] . \tag{12b}$$

The steps leading to Eq. (12b) are given in the Appendix. Only a small amount of algebra is then required to obtain the complete form of the wave function in momentum space by substituting Eqs. (12a) and (12b) into Eq. (10).

Having obtained the off-shell wave function, one can arrive at the form of the fully-off-shell T-matrix elements by first rewriting Eq. (1) as

$$H\Omega(E^+) = E[\Omega(E^+)-I]+H_0 . \tag{13}$$

It follows from the definition of the transition operator and from the above equation that

$$T(E^+)=V\Omega(E^+)=(H-H_0)\Omega(E^+)$$
$$=(E-H_0)[\Omega(E^+)-I] \ . \tag{14}$$

One thus obtains for the off-shell T-matrix elements:

$$\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle=\frac{1}{2\mu}(p_E^2-p'^2)[\langle \mathbf{p}'|\Omega(E^+)|\mathbf{p}\rangle - \delta(\mathbf{p}'-\mathbf{p})] \ , \tag{15}$$

which indicates that the momentum representation of the Møller operator is in fact the off-shell wave function in momentum space. The off-shell T-matrix elements can also be written in partial wave form:

$$\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle=\frac{1}{4\pi}\sum_{l=0}^{\infty}(2l+1)P_l(\hat{\mathbf{p}}'\cdot\hat{\mathbf{p}})t_l(p',p;E^+) \ , \tag{16}$$

where $t_l(p',p;E^+)$ are partial-wave off-shell T- matrix elements. By inserting the above equation, as well as the expression for the wave function in momentum space, into Eq. (15), and comparing both sides, one obtains the final result for the fully-off-shell T-matrix elements:

$$\begin{aligned} t_l(p',p;E^+)=\frac{1}{\pi\mu p p'}\Bigg[& \frac{\alpha_l(p_E^2-p'^2)}{p'^2-q^2}\Bigg\{p'\left[\hat{j}_l\left[\frac{qa}{\hbar}\right]\hat{j}_{l-1}\left[\frac{p'a}{\hbar}\right]-\hat{j}_l\left[\frac{qb}{\hbar}\right]\hat{j}_{l-1}\left[\frac{p'b}{\hbar}\right]\right] \\ & +q\left[\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{p'b}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{p'a}{\hbar}\right]\right]\Bigg\} \\ & +\frac{\beta_l(p_E^2-p'^2)}{p'^2-q^2}\Bigg\{q\left[\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{p'b}{\hbar}\right]-\hat{h}_{l-1}^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{p'a}{\hbar}\right]\right] \\ & +p'\left[\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_{l-1}\left[\frac{p'a}{\hbar}\right]-\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_{l-1}\left[\frac{p'b}{\hbar}\right]\right]\Bigg\} \\ & +\frac{(p_E^2-p'^2)(p_E^2-p^2)}{(q^2-p^2)(p'^2-p^2)}\Bigg\{p\left[\hat{j}_l\left[\frac{p'b}{\hbar}\right]\hat{j}_{l-1}\left[\frac{pb}{\hbar}\right]-\hat{j}_l\left[\frac{p'a}{\hbar}\right]\hat{j}_{l-1}\left[\frac{pa}{\hbar}\right]\right] \\ & +p'\left[\hat{j}_{l-1}\left[\frac{p'a}{\hbar}\right]\hat{j}_l\left[\frac{pa}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{p'b}{\hbar}\right]\hat{j}_l\left[\frac{pb}{\hbar}\right]\right]\Bigg\} \\ & +\frac{p_E^2-p'^2}{p^2-p'^2}\left[p\hat{j}_{l-1}\left[\frac{pb}{\hbar}\right]\hat{j}_l\left[\frac{p'b}{\hbar}\right]-p'\hat{j}_{l-1}\left[\frac{p'b}{\hbar}\right]\hat{j}_l\left[\frac{pb}{\hbar}\right]\right] \\ & +\gamma_l\left[p_E\hat{j}_l\left[\frac{p'b}{\hbar}\right]\hat{h}_{l-1}^{(1)}\left[\frac{p_Eb}{\hbar}\right]-p'\hat{j}_{l-1}\left[\frac{p'b}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{p_Eb}{\hbar}\right]\right]\Bigg] \ , \end{aligned} \tag{17}$$

where we have made use of the partial-wave expansion for the three-dimensional δ function.

We next verify that the above results satisfy the analytic properties known for the off-shell T matrix for any spherical potential.[10] Equation (16) indicates that one only needs to examine the partial-wave T-matrix elements $t_l(p',p;E^+)$.

(1) *Symmetry.* One can readily show from Eq. (17) that

$$\begin{aligned} t_l(p',p;E^+)-t_l(p,p';E^+)=\Bigg\{ & \left[\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{qb}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]\right] \\ & -\left[\hat{h}_{l-1}^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{qa}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{qa}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\right]\Bigg\}f_l(p,p';E) \ , \end{aligned} \tag{18}$$

where $f_l(p,p';E)$ is a well-behaved function of p and p'. However, each of the expressions between square brackets is equal to i, and they therefore cancel each other. As a result, the right-hand side of Eq. (18) is zero, and consequently

$$t_l(p',p;E^+)=t_l(p,p';E^+) \ , \tag{19}$$

as was expected.[10]

(2) *Half-off-shell limit.* When one sets $p'\rightarrow p_E$ in Eq. (17), the fully-off-shell T matrix then reduces to the half-off-shell case. As we have pointed out, the half-off-shell T matrix is related to the wave function through the equation

$$t_l(p,p_E;E^+)=\frac{i\gamma_l}{\pi\mu p} \ , \tag{20}$$

where γ_l is given by Eq. (8c).

(3) *On-shell limit.* When one sets $p\rightarrow p_E$ in Eq. (20), then one obtains the on-shell T matrix. If one further takes $V_0\rightarrow 0$, then t_l reduces to the form

$$t_l(p_E,p_E;E^+)=-\frac{i}{\pi\mu p_E}\frac{\hat{j}_l(p_E a/\hbar)}{\hat{h}_l^{(1)}(p_E a/\hbar)}\ , \tag{21}$$

from which the well-known expression of the scattering phase shift for the hard-core potential is readily obtained.

(4) *Unitarity.* Combining the above results, one can easily verify that the present fully-off-shell T-matrix elements satisfy the unitarity condition

$$\mathrm{Im}\,t_l(p',p;E^+)=-\pi\mu p_E t_l^*(p',p_E;E^+)t_l(p,p_E;E^+)\ , \tag{22}$$

which is the off-shell analog of the optical theorem.

(5) *Bound states.* For the sake of completeness, we note that the above expressions can also be used to determine the bound states of the model potential. As is well known, the bound states correspond to the poles of the T matrix evaluated for imaginary values of p_E. Making the appropriate substitutions (i.e., $p_E\rightarrow i\kappa$, where $\kappa=\sqrt{2\mu|E|}$) in the denominator of the T matrix given by Eqs. (9) and (17), one readily finds that the bound-state energies, $E_n=-\kappa_n^2/2\mu$ ($n=0,1,2,\dots$), are determined by the roots κ_n of the following equation:

$$q\hat{h}_l^{(1)}\left[\frac{i\kappa b}{\hbar}\right]\left[\hat{h}_{l-1}^{(1)}\left[\frac{qb}{\hbar}\right]\hat{j}_l\left[\frac{qa}{\hbar}\right]-\hat{j}_{l-1}\left[\frac{qb}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\right]$$
$$+i\kappa\hat{h}_{l-1}^{(1)}\left[\frac{i\kappa b}{\hbar}\right]\left[\hat{h}_l^{(1)}\left[\frac{qa}{\hbar}\right]\hat{j}_l\left[\frac{qb}{\hbar}\right]-\hat{j}_l\left[\frac{qa}{\hbar}\right]\hat{h}_l^{(1)}\left[\frac{qb}{\hbar}\right]\right]=0\ , \tag{23}$$

which can be solved numerically for the κ_n, for example, by Newton's method.

III. COMPUTATIONAL PROCEDURE

The off-shell T matrix is a well-behaved function of $\mathbf{p}$ and $\mathbf{p}'$ when the energy E is positive. From Eqs. (9) and (17) it would appear that the T matrix has singularities when the denominators go to zero. However, it is straightforward to show that in those cases the corresponding numerators also go to zero in a way such that the T matrix remains finite. When attempting to calculate t_l from Eq. (17), certain care must be taken to avoid possible overflows due to the fact that the Hankel functions increase very rapidly for large values of l. However, the denominator of t_l increases much faster than its numerator as l increases, so that one can take advantage of this behavior to avoid overflows. In practice, it is also convenient to fully expand Eq. (17) and then regroup the terms in a way such that each h_l is multiplied by the corresponding $\hat{j}_l$ of the same argument. As a consequence, the products $\hat{j}_l\hat{h}_l$ will then remain within the dynamic range of the computer. Inspecting Eqs. (8), (9), and (17), one finds that the expansion will involve a large number of terms. Therefore, it is most reliably carried out by means of a symbolic manipulation program such as MACSYMA.[14]

The necessary Ricatti-Bessel functions $\hat{j}_l$ and $\hat{h}_l$ are obtained by standard numerical procedures[13,15] as follows. It is well known that the recursion relation for the $\hat{j}_l$ is unstable for increasing values of l. Therefore, given the desired value x of the argument, we first calculate $l_{\max}$ such that $[\hat{j}_l(x)|<\epsilon$ for $l>l_{\max}$, where ϵ is a small number, typically $\epsilon=10^{-35}$. More specifically, $l_{\max}$ is determined from the relation

$$l_{\max}=x+2(-\tfrac{2}{3}\ln 10^{-20}\sqrt{x/2})^{2/3}\ , \tag{24}$$

which follows from the asymptotic expansion[12] of $\hat{j}_l$ for large l:

$$\hat{j}_l(x)\sim\left[\frac{x}{2(2l+1)}\right]^{1/2}\left[\frac{ex}{2l+1}\right]^{l+1/2}. \tag{25}$$

We next apply the recursion relation[12]

$$\hat{j}_{l-2}(x)=\frac{2l-1}{x}\hat{j}_{l-1}(x)-\hat{j}_l(x) \tag{26}$$

downwards from $l=l_{\max}$ to $l=0$, and then normalize the resulting $\hat{j}_l(x)$. Instead, the recursion relation for the Ricatti-Neumann functions $\hat{n}_l(x)$ is known to be stable, so we first write $\hat{h}_l=\hat{j}_l+i\hat{n}_l$, and then generate the $\hat{n}_l$ by forwards recursion as follows:

$$\hat{n}_{l+2}(x)=\frac{2l+3}{x}\hat{n}_{l+1}(x)-\hat{n}_l(x)\ . \tag{27}$$

It is worth noting that the above procedure is sufficiently inexpensive to generate Bessel functions for large values of l, typically $l\sim 1000$. As a consequence, we can easily examine the convergence of the T matrix with respect to the number of partial waves included in the calculation. Whenever p and p' are near the energy shell, we have found that the T matrix converges when the number of partial waves approaches the classical estimate $L=p_E b$, as was expected. However, when p and/or $p'\ll p_E$, then the convergence is faster, because each partial wave is dominated by $\hat{j}_l(pb/\hbar)\hat{j}_l(p'b/\hbar)$ [cf. Eq. (17)] and the Recatti-Bessel functions decrease more rapidly for smaller argument. Conversely, for the same reason, one requires more partial waves than L in order for the T matrix to converge when p and/or $p'\gg p_E$. However, in the latter case the amplitude of the T matrix is significantly smaller, because Eq. (17) indicates that $t_l(p',p;E^+)\propto 1/pp'$ as p and/or p' becomes large.

The calculations for the off-shell T matrix are performed on Microvax 3100 works stations. Typically, for $E=1$ eV, $p=0.4p_E$, and $p'=0.6p_E$, it takes about 3 sec of CPU time to calculate the T matrix as a function of the angle between $\mathbf{p}$ and $\mathbf{p}'$ from 0° to 180° in steps of 1° with approximately 110 partial waves included.

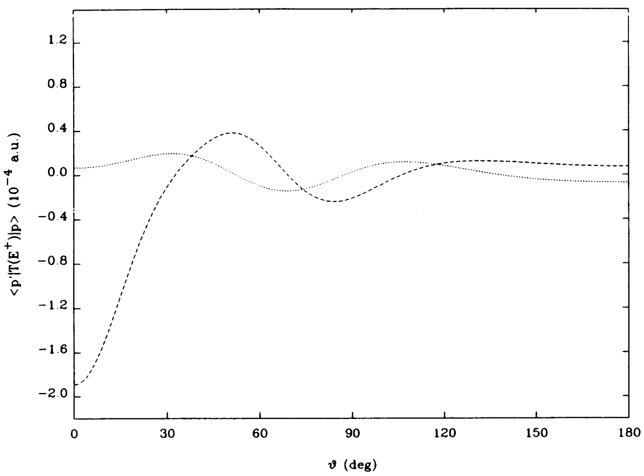

FIG. 1. Off-shell T matrix for $p=0.4p_E$ and $p'=0.6p_E$ at $E=30$ meV. $a=1.75$ Å, $b=3.0$ Å, and $V_0=3$ meV. Dashed line $\mathrm{Re}\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$; dotted line, $\mathrm{Im}\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$.

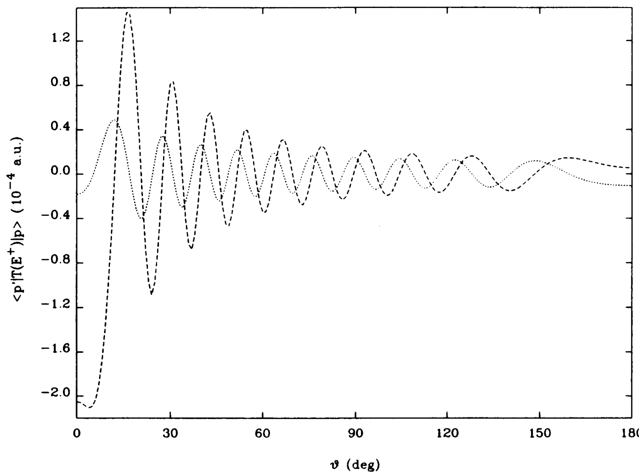

FIG. 3. Same as Fig. 1 except $E=1.0$ eV.

IV. EXAMPLES

To illustrate the behavior of the fully-off-shell T matrix, we have carried out calculations for several values of energy and momenta using potential parameters that simulate typical interactions between noble-gas atoms: $V_0=3$ meV, $a=1.75$ Å, and $b=3.0$ Å; the mass of helium was used in the calculations. As was mentioned in the first section, the behavior of the off-shell T matrix strongly depends on the three independent quantities: $\mathbf{p}$, $\mathbf{p}'$, and E. Qualitatively speaking, Eqs. (8), (9), and (17) lead one to expect that the T matrix will vary slowly for small values of the independent variables, and that it will become progressively more oscillatory as the independent variables increase, since $\mathbf{p}$, $\mathbf{p}'$, and p_E appear as multiplicative parameters in the arguments of the Bessel functions. This behavior is illustrated by Figs. 1–3, where we display the fully-off-shell T matrix versus the angle between $\mathbf{p}$ and $\mathbf{p}'$ for three different values of energy E such that $p_E > p,p'$. As in the well-known on-shell case, one sees that the amplitude of the T matrix varies more rapidly in the small-angle region, and that it becomes progressively more oscillatory as E increases from 0.03 to 0.3 to 1.0 eV, respectively, in Figs. 1–3. One also notes that the magnitude of the T matrix on average does not change much even when E is varied over almost 2 orders of magnitude while keeping constant the magnitudes of the momenta. Next, Fig. 4 illustrates the effect of reducing the magnitudes of the momenta at the larger energy ($E=1.0$ eV); one sees that the T matrix becomes less oscillatory as was expected. Conversely, Fig. 5 shows a case of relatively low-energy $E=30$ meV but large off-shell momenta $p=3.5p_E$ and $p'=4p_E$; here the T matrix oscillates rapidly, and its magnitude decreases very quickly as the angle increases. In fact, the magnitude of the T matrix becomes progressively smaller as one increases p and/or p', and it eventually vanishes. These examples illustrate the strong influence of the momenta on

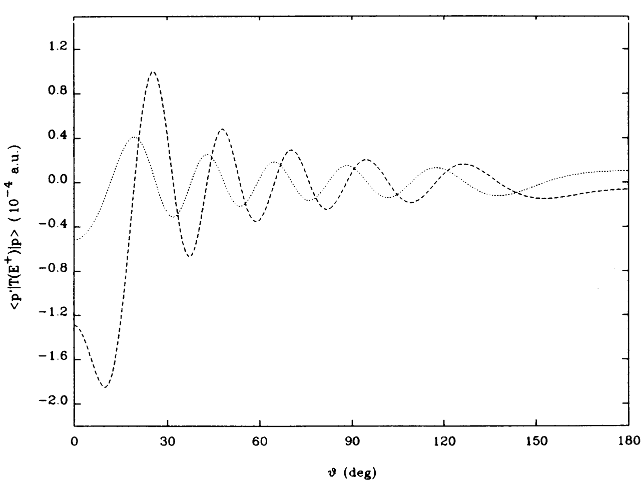

FIG. 2. Same as Fig. 1 except $E=300$ meV.

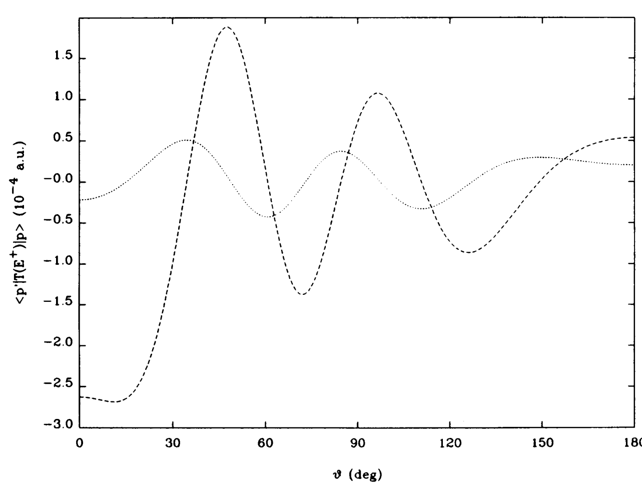

FIG. 4. Same as Fig. 3 except $p=0.1p_E$ and $p'=0.3p_E$.

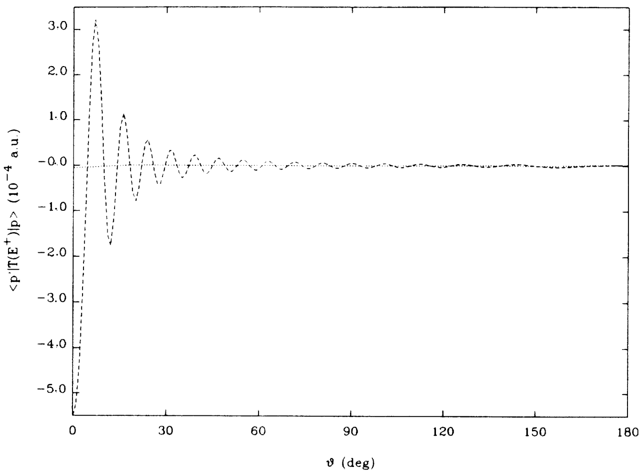

FIG. 5. Same as Fig. 1 except $p=3.5p_E$ and $p'=4.0p_E$.

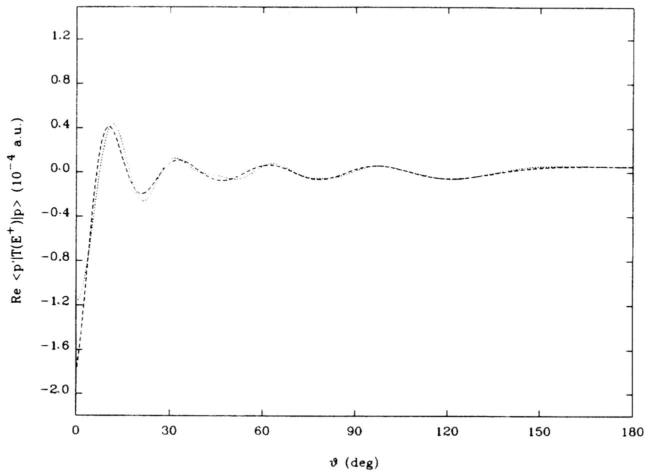

FIG. 7. $\mathrm{Re}\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$. Dotted line, square-well potential with $a=1.75$ Å and $b=3.0$ Å; dashed line, Lennard-Jones potential with $r_m=2.0$ Å. Here the results are on shell with $e=30$ meV and $V_0=3$ meV.

the behavior of the off-shell T matrix.

Finally, we examine how the T matrix varies as one changes the potential parameters (presently, the radii a and b and the well depth V_0). Qualitatively, one would expect the T matrix to varies slowly with angle when a and b are small, and to become more oscillatory as the radii increase, since these two parameters also appear as multiplicative constants within the arguments of the Bessel functions. These expectations are confirmed by comparing Fig. 1 with Fig. 6, where the T matrix has been calculated with a larger value of the hard-core radius. Considering next the well depth, it is known that the ratio E/V_0 plays an important role in determining the behavior of two-body cross sections. Hence Figs. 7 and 8 compare results obtained from the model potential with those of a Lennard-Jones (12,6) potential, both calculated on shell with $E/V_0=10$. It is seen that the T matrices closely resemble each other, while the significant differences occur mainly at small angles due to the longer range of the Lennard-Jones potential. The close resemblance over a wide range of scattering angles leads one to expect that the model potential will yield meaningful results when its T matrix is incorporated into the integrals arising in multiple-collision expansions, provided that the impact energy is considerably higher than the typical well depths.

V. SUMMARY

We have obtained an analytic and explicit expression for the fully-off-shell T-matrix elements for the spherical hard-core plus square-well potential. Similar approaches can be applied to piecewise-constant potentials, although the resulting expressions become much more complicated.[9] The results shown in Figs. 7 and 8 suggest that the present potential can be used to model more realistic (i.e.,

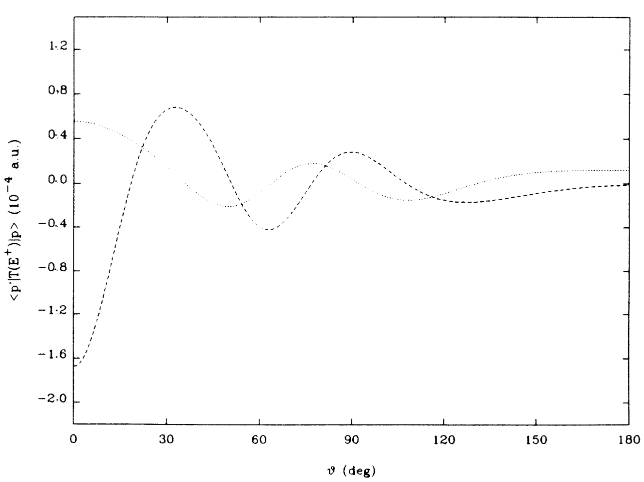

FIG. 6. Same as Fig. 1 except $a=2.25$ Å and $b=3.5$ Å.

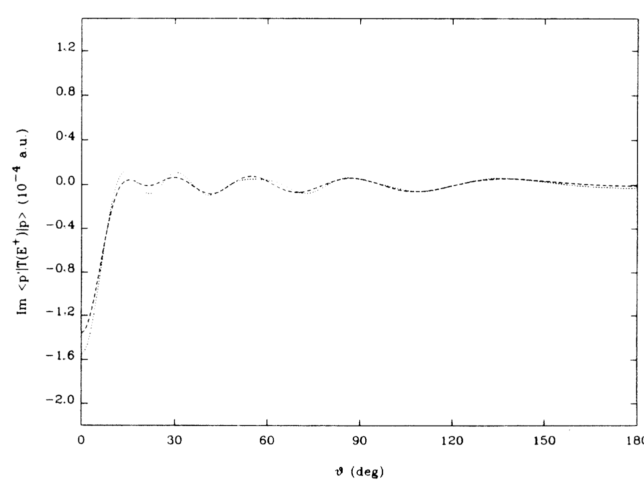

FIG. 8. Similar to Fig. 7, but for $\mathrm{Im}\langle \mathbf{p}'|T(E^+)|\mathbf{p}\rangle$.

continuous) interatomic forces at sufficiently high collision energies. Hence the present T matrix is expected to provide a computationally efficient approximation for use in multiple-scattering theory within the high-collisional-energy regime. In particular, these analytic results make possible the calculation of multiple-collision terms describing certain classes of reactive collisions, such as collision-induced dissociation and desorption. In a series of separate papers,[4] we combine these results together with multiple-scattering theory to investigate such reactive processes both in the gas phase and at the gas-solid interface.

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APPENDIX

Equation (12a) can be found in any standard text book.[12] We only give a brief proof of Eq. (12b) in this section. In order to do this, two integrals are needed.

Integral 1. Define a cylinder function by

$$W_\nu(x)=\sigma[J_\nu(x)\cos\alpha+Y_\nu(x)\sin\alpha] , \tag{A1}$$

where ν is a non-negative number and σ and α are real constants. We have that

$$\int_b^\infty W_\nu(sx)W_\nu(tx)x\,dx =\frac{\sigma^2}{s}\delta(s-t)-\frac{b}{s^2-T^2}[sW_{\nu+1}(sb)W_\nu(tb) -tW_{\nu+1}(tb)W_\nu(sb)] . \tag{A2}$$

This equation can be easily proven by taking into account Weber's integral theorem,[17] as well as the equation for the same integrand in a finite range:

$$\int_b^\lambda W_\nu(sx)W_\nu(tx)x\,dx=\frac{1}{s^2-t^2}\{\lambda[sW_{\nu+1}(s\lambda)W_\nu(t\lambda)-tW_{\nu+1}(t\lambda)W_\nu(s\lambda)] -b[sW_{\nu+1}(sb)W_\nu(tb)-tW_{\nu+1}(tb)W_\nu(sb)]\} . \tag{A3}$$

Equation (12a) is, in fact, a specific case of the more general expression (A2).

Integral 2. Letting

$$U_\nu(x)=Y_\nu(bs)J_\nu(x)-J_\nu(bs)Y_\nu(x) ,\quad \tilde{U}_\nu(x)=Y_\nu(bt)J_\nu(x)-J_\nu(bt)Y_\nu(x) , \tag{A4}$$

then

$$\int_b^\infty U_\nu(sx)\tilde{U}_\nu(tx)x\,dx=\frac{1}{s}[J_\nu^2(bs)+Y_\nu^2(bs)]\delta(t-s) . \tag{A5}$$

This can be readily proven with the Weber form.[13] Combining the two integrals, one can show that

$$\int_b^\infty \hat{j}_l\left(\frac{p'r}{\hbar}\right)\hat{y}_l\left(\frac{pr}{\hbar}\right)dr =\frac{\hbar}{p^2-p'^2}\left[p'\hat{j}_{l+1}\left(\frac{p'b}{\hbar}\right)\hat{y}_l\left(\frac{pb}{\hbar}\right) -p'\hat{j}_l\left(\frac{p'b}{\hbar}\right)\hat{y}_{l+1}\left(\frac{pb}{\hbar}\right)\right] . \tag{A6}$$

Equation (12b) can then be derived easily from Eqs. (12a) and (A6).

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