SCATTERING AMPLITUDES FOR REARRANGEMENT PROCESSES AT LOW ENERGIES

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Translated from Doklady Akademii Nauk SSSR, Vol. 182, No. 5, pp. 1036-1039, October, 1968
Original article submitted June 28, 1968

In the present paper we have considered the possibility of deriving expressions for the amplitude for rearrangement processes from the general quantum mechanical theory of multiparticle scattering for the case in which the kinetic energy of the dispersed fragments is small compared to the excitation energy of their highest levels. Such cases occur in various inelastic atom-molecule collisions as well as in chemical reactions and low-energy nuclear reactions. We represent the scattering process with rearrangement (reaction) in the steady state symbolically in the following way:

$$(1, 2) + 3 \to 1 + (2, 3), \qquad (1)$$

where 1, 2, and 3 are, generally speaking, complex fragments,[1] and the parentheses designate the bound state.

We denote the initial reaction channel by the index i, and the final one by the index f; the other channels may here be regarded as closed. We introduce in the center-of-mass system two equivalent sets of Jacobi coordinates: first the set i, which includes the radius vector $\mathbf{R}_i$ joining the mass centers (1, 2) and 3, the radius vector $\mathbf{r}_i$ joining the mass centers 1 and 2, and $\vec{\xi}_i$, which is the totality of the remaining "internal coordinates". The other set f includes $\mathbf{R}_f$, $\mathbf{r}_f$, and is analogous to the set i with a permutation $1 \leftrightarrow 3$. The total mass of the system is $M = m_1 + m_2 + m_3$. We relate the reduced masses, $M_i = m_3(m_1 + m_2)/M$ and $M_f = m_1(m_2 + m_3)/M$, respectively, to the motion along the coordinates $\mathbf{R}_i$ and $\mathbf{R}_f$, and the reduced masses $m_i = m_1m_2/(m_1 + m_2)$ and $m_f = m_2m_3/(m_2 + m_3)$ to the motion along the coordinates $\mathbf{r}_i$ and $\mathbf{r}_f$, respectively. The total Hamiltonian $\mathcal{H}$ of the system may be decomposed by the two following methods:

$$\mathcal{H} = \mathcal{K}_\alpha + \mathcal{H}_\alpha = (\mathcal{K}_\alpha + h_\alpha) + V_\alpha \quad (\alpha = i, f), \qquad (2)$$

where $\mathcal{K}_\alpha$ is an operator of the kinetic energy of motion along $\mathbf{R}_\alpha$, and V_α is an interaction part which goes to zero for $\mathbf{R}_\alpha \to \infty$. The asymptotic states (for $\mathbf{R}_\alpha \to \infty$) of the problem under consideration are eigenfunctions of $(\mathcal{K}_\alpha + h_\alpha)$, and are given by the following functions:

$$\Phi_{\alpha n\mathbf{k}}(\mathbf{R}_\alpha, \mathbf{r}_\alpha, \vec{\xi}_\alpha) = \sqrt{M_\alpha/k_\alpha}, \quad e^{i\mathbf{k}_\alpha \mathbf{R}_\alpha}\varphi_{\alpha n}(\mathbf{r}_\alpha\vec{\xi}_\alpha), \qquad (3)$$

Here $\varphi_{\alpha n}$ (taken as real numbers) are normalized functions of the bound states representing eigenfunctions of the discrete spectrum of the operator h_α with the eigenvalue $\mathcal{E}_{\alpha n}$, and on the energy surface

$$k_\alpha^2/2M_\alpha + \mathcal{E}_{\alpha n} = E. \qquad (4)$$

The asymptotic state is thus characterized not only by the channel index $\alpha = i, f$, but also by the value of the momentum $\mathbf{k}_\alpha$ and by the index n, which characterizes the quantum numbers of the bound state.

As in [2] we now introduce the functions $\psi_{\alpha n}(\mathbf{r}_\alpha, \vec{\xi}_\alpha; \mathbf{R}_\alpha)$, which are eigenfunctions of $\mathcal{H}_\alpha$ depending on $\mathbf{R}_\alpha$ as well as on the parameter:

$$\begin{gathered}\mathcal{H}_\alpha \psi_{\alpha n}(\mathbf{r}_\alpha, \vec{\xi}_\alpha; \mathbf{R}_\alpha) = \mathcal{E}_{\alpha n}(\mathbf{R}_\alpha)\psi_{\alpha n}(\mathbf{r}_\alpha, \vec{\xi}_\alpha; \mathbf{R}_\alpha), \\ \psi_{\alpha n}(\mathbf{r}_\alpha; \vec{\xi}_\alpha; \mathbf{R}_\alpha) \xrightarrow[R_\alpha \to \infty]{} \varphi_{\alpha n}(\mathbf{r}_\alpha, \vec{\xi}_\alpha), \quad \mathcal{E}_{\alpha n}(\mathbf{R}_\alpha) \to \mathcal{E}_{\alpha n}, \\ (\psi_{\alpha n'}, \psi_{\alpha n})_\alpha \equiv \int \psi_{\alpha n'}\psi_{\alpha n}(d\mathbf{r}_\alpha)(d\vec{\xi}_\alpha) = \delta_{n'n}.\end{gathered} \qquad (5)$$

We introduce the operators $\Pi_{\alpha n}$ of projection into the space $\mathbf{r}_\alpha$, $\vec{\xi}_\alpha$: $\Pi_{\alpha n}\Psi = \psi_{\alpha n}(\psi_{\alpha n}, \Psi)_\alpha$. Furthermore, we derive from $\Pi_{\alpha n}$ the operators $\Pi_\alpha = \sum_{n=0}^{n_{max}} \Pi_{\alpha n}$ where the summation with respect

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[1] In the case of identical particles the definition of the reaction channels and asymptotic functions is generalized in a trivial fashion according to [1].

to n runs from the ground state n = 0 to some finite n_{max}, which may be determined for a given problem by means of the condition[2] given below. Introducing also the operators $\Sigma_\alpha = 1 - \Pi_\alpha$ we have

$$\Pi_\alpha\Sigma_\alpha = \Sigma_\alpha\Pi_\alpha = 0, \quad \Pi_\alpha\mathcal{H}\Sigma_\alpha = \Pi_\alpha\mathcal{H}_\alpha\Sigma_\alpha \quad (\alpha = i, f). \tag{6}$$

We designate by $\Psi^{\pm}_{\alpha nk}$ the complete solutions (obtained for $\Phi_{\alpha nk}$) of the scattering problem in the steady state with converging and diverging waves [3], respectively. For the determination of elastic scattering as well as of scattering with transitions between the discrete states ($n \leq n_{max}$) in one reaction channel it is sufficient to determine $\tilde{\Psi}^{\pm}_{\alpha nk} = \Pi_\alpha\Psi^{\pm}_{\alpha nk}$ ($n \leq n_{max}$).

The functions $\tilde{\Psi}^{\pm}_{\alpha nk}$ are inserted into the following equations ($\varepsilon \to +0$ in all cases):

$$\Pi_\alpha\left[(H-E) + \mathcal{H}_\alpha\Sigma_\alpha\frac{1}{\Sigma_\alpha(E-H\pm i\varepsilon)\Sigma_\alpha}\Sigma_\alpha\mathcal{H}_\alpha\right]\Pi_\alpha\tilde{\Psi}^{\pm}_{\alpha nk} \equiv (H-E+\Delta^{\pm}_\alpha)\tilde{\Psi}^{\pm}_{\alpha nk} = 0,$$

$$\Delta^{\pm}_\alpha = [\Pi_\alpha, \mathcal{H}_\alpha] + [\Pi_\alpha, \mathcal{H}_\alpha]\Sigma_\alpha\frac{1}{\Sigma_\alpha(E\pm i\varepsilon-H)\Sigma_\alpha}\Sigma_\alpha[\mathcal{H}_\alpha, \Pi_\alpha]. \tag{7}$$

The functions introduced may be written in the following form:

$$\Psi^{\pm}_{\alpha nk} = \sum_{n'=0}^{n_{max}} y^{I}_{n', \alpha nk'}(\mathbf{R}_\alpha)\,\psi_{\alpha n'}(\mathbf{r}_\alpha, \vec{\xi}_\alpha; \mathbf{R}_\alpha),$$

where the summation with respect to n' runs over the range from n' = 0 to n_{max}.[3]

Using the same operational algebra as in [5] for the derivation of the equation for perturbed waves, and allowing for the finiteness of $(\Phi_{\alpha n'k'}, \Psi_{\alpha nk})$ for $\alpha' \neq \alpha$, we obtain the following expression for the T-matrix of rearrangement:

$$T_{\alpha'n'k', \alpha nk} = (\Psi^{-}_{\alpha'n'k}, \left[-\Delta^{+}_\alpha + (\Delta^{-}_{\alpha'})^*\frac{1}{E-H+i\varepsilon}\Delta^{+}_\alpha\right]\Psi^{+}_{\alpha nk}), \tag{8}$$

where the asterisk designates the Hermitian adjoint. We obtain an alternative solution from (8) by replacing the first term in the square brackets by $-(\Delta_{\alpha'^-})^*$. Eq. (8) may be rewritten as follows:

$$T_{\alpha'n'k, \alpha nk} = (\tilde{\Psi}^{-}_{\alpha'n'k'}, \tilde{u}_{\alpha', \alpha}\tilde{\Psi}^{+}_{\alpha nk}), \tag{9}$$

where

$$\tilde{u}_{\alpha'\alpha} = -\Pi_{\alpha'}\Big(1 + [\Pi_{\alpha'}, \mathcal{H}_{\alpha'}] \times \Sigma_{\alpha'}\frac{1}{\Sigma_{\alpha'}(E+i\varepsilon-\mathcal{H})\Sigma_{\alpha'}}\Sigma_{\alpha'}\Big)[\Pi_\alpha, \mathcal{H}_\alpha] \times\Big(1 + \Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H})\Sigma_\alpha}\Sigma_\alpha[\mathcal{H}_\alpha, \Pi_\alpha]\Big)\Pi_\alpha. \tag{10}$$

The quantities $\mathcal{G}(\Sigma_\alpha) = \Sigma_\alpha[\Sigma_\alpha(E + i\varepsilon - \mathcal{H})\Sigma_\alpha]^{-1}\Sigma_\alpha$ are of great importance in Eq. (10); they are defined by the integral equation

$$\mathcal{G}(\Sigma_\alpha) = \Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H}_\alpha)\Sigma_\alpha}\Sigma_\alpha + \Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H}_\alpha)}\Sigma_\alpha\mathcal{H}_\alpha\Sigma_\alpha\mathcal{G}(\Sigma_\alpha). \tag{11}$$

Here

$$\Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H}_\alpha)\Sigma_\alpha}\Sigma_\alpha = \sum_{n>n_{max}}\Pi_{\alpha n}(E+i\varepsilon-\mathscr{E}_{\alpha n}), \tag{12}$$

where the summation with respect to n is taken over the whole spectrum $\mathcal{H}_\alpha$ for $n > n_{max}$.

We assume that we can choose n_{max} in such a way that $E - \mathscr{E}_{\alpha n}(\mathbf{R}) \equiv \frac{k^2_{\alpha 0}}{2M_\alpha} - (\mathscr{E}_{\alpha n}(\mathbf{R}) - \mathscr{E}_{\alpha 0}) \ll 0$ for $n > n_{max}$ and all values of $\mathbf{R}_\alpha$ contained in the expression for the T-matrix.

At low energies the substitution of the solutions of Eq. (11) by means of the iterations in Eqs. (9) and (10) gives the decomposition for the T-matrix of rearrangement with respect to the following parameter:

$$\max\frac{\|[\mathcal{H}_\alpha, \Pi_\alpha]\Pi_\alpha\|}{|\mathscr{E}_{\alpha n}(\mathbf{R}) - \mathscr{E}_{\alpha 0}|}, \quad n > n_{max}. \tag{13}$$

When the motion described by Eq. (8) can still be regarded as quasiclassical, this parameter transforms to $\max \hbar k_{\alpha 0}/2M\lambda|\mathscr{E}_{\alpha n}(\mathbf{R}) - \mathscr{E}_{\alpha 0}|$ ($n > n_{max}$), where λ is the characteristic distance for

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[2] We assume that for $n \leq n_{max}$ the functions $\mathscr{E}_{\alpha n}(\mathbf{R})$ (for an identical symmetry of the functions $\psi_{\alpha n}$, which has been allowed for in the index n) do not overlap. In fact there may be overlapping, a case demanding special attention [2]; for point centers $\mathscr{E}_{\alpha n}(\mathbf{R})$ in fact depends only on two factors: One of the angles determining R in spherical coordinates is not contained in $\mathscr{E}_{\alpha n}(\mathbf{R})$.

[3] For $y_{n', \alpha nk}$ we can write the following set of equations and boundary conditions:

$$[\mathcal{H}_\alpha - (\mathscr{E}_{\alpha n}(\mathbf{R}) - \mathscr{E}_{\alpha n}) - (E - \mathscr{E}_{\alpha n})]\,y^{\pm}_{n,\,\alpha k}(\mathbf{R}_\alpha) = -\sum_{n=0}^{n_{max}}\{[(\psi_{\alpha n}, [\mathcal{H}_\alpha, \psi_{\alpha n'}])_\alpha - (\psi_{\alpha n}, \mathcal{H}_\alpha\Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H})\Sigma_\alpha}\Sigma_\alpha\mathcal{H}_\alpha\psi_{\alpha n'})_\alpha]y_{n', \alpha nk'}(\mathbf{R}_\alpha),$$

$$y_{n', \alpha nk} \xrightarrow[R_\alpha\to\infty]{} \delta_{n'n}\sqrt{k_\alpha/M_\alpha}\exp(i\mathbf{k}_\alpha\mathbf{R}_\alpha) + f_{n'n}(\mathbf{k}_\alpha\mathbf{k}'_\alpha)\exp(\pm i|\mathbf{k}'_\alpha|\mathbf{R}_\alpha)/R_\alpha,$$

where $\mathbf{k}_{\alpha'^2}$ lies on the energy surface. The determination of $y_{\alpha', \alpha n}$ is equivalent to the, in principle, available solution of the problem of potential scattering with a finite discrete number of internal states and a rather rapidly decreasing nonlocal and complex potential.

the reduction of the influence of the third particle on the bound state of the two other particles in the channels i and f. It can be easily seen that the latter parameter is equivalent to that contained in Massey's criterion [6] of energy level excitation for $n > n_{max}$. Then the first term T^0 of the above decomposition is equal in the general case to

$$T^0_{\alpha' n' k', \alpha n k} = -(\tilde{\Psi}^-_{\alpha' n' k'} [\Pi_a, \mathscr{K}_a] \tilde{\Psi}^+_{\alpha n k}). \qquad (14)$$

The first nonzero terms of similar decompositions are, as a matter of fact, used in numerous approximation methods. They are of special interest in various fields referring to the quasiadiabatic, quasimolecule, transition-complex, and quasi- (or direct) resonance (for charge transfer) methods [6]. In the latter case it is sometimes thought possible to consider the functions $\psi_{\alpha' n'}$ and $\psi_{\alpha n}$ derived from different channels in the reaction region as the eigenfunctions of an approximate Hamiltonian (e.g., when the second particle is far lighter than the others). In this case the first term of the decomposition in Eq. (14) becomes zero. This seems reasonable, since the formation of collision complexes from heavy particles (Breit-Wigner resonances), which depends strongly on the kinetic energy and corresponds to the passages of the phase through $k\pi/2$ (classical detention) can be represented (for "smooth" elastic scattering) only in the subsequent terms of the T-matrix having energy-dependent demoninators.

We must emphasize here that, as may be easily checked, the kernel of the integral equation (11) is not completely continuous [7]. Thus the use of the simple iterational decomposition without rearrangement of the kernel may lead to qualitatively erroneous conclusions. This fact is evidently the reason that certain reactions go rapidly when this is contrary to Massey's criterion [7].

It is another important characteristic of the expressions obtained from the matrix of rearrangement that the expressions of the type (14) have sharp maxima simultaneous with the maxima of the overlap integral $(\tilde{\Psi}^-_{\alpha' n' k}, \tilde{\Psi}^+_{\alpha n k}) = (y^-_{\alpha' n' k'} \psi_{\alpha' n'}, y_{\alpha n k} \psi_{\alpha n})$. The latter maxima for $\alpha' \neq \alpha$ are not related to any collision complexes and correspond to wave resonances of the non-Breit-Wigner type. These resonances correspond to the optimum correlation of motions (quasiclassical in atom-molecule collisions) along the coordinates R_i and R_f with internal, essentially quantum, motions. The consequences of the existence of such a correlation have been considered in [9] for the specific case of chemical reactions.

In conclusion we may remark that the above considerations allow the expression of the probability of reactions in terms of the characteristics of the asymptotic states and elastic scattering, without the interaction potentials being explicitly given.

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