SCATTERING AMPLITUDES WITH REARRANGEMENT AT LOW ENERGIES

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Abstract

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The paper considers the possibility of deriving, from the general quantum-mechanical theory of many-particle scattering, an expression for the amplitude of a process with rearrangement in the case when the kinetic energy of the outgoing fragments is small compared with the excitation energy of their higher levels. Such cases occur in various inelastic atomic–molecular collisions, in chemical reactions, and also in nuclear reactions at low energies. We shall symbolically represent the stationary problem of the scattering process with rearrangement (reaction) at energy equal to E by the scheme

$$(1,2)+3 \to 1+(2,3), \tag{1}$$

where 1, 2, and 3 are, generally speaking, composite fragments,* and the parentheses denote a bound state. We shall denote the initial channel of the reaction by the index i, and the final one by the index f. The other channels will here be considered closed. We introduce, in the center-of-mass system, two equivalent sets of Jacobi coordinates: first, the set i, including $\mathbf{R}_i$—the radius vector connecting the centers of mass of $(1,2)$ and 3, $\mathbf{r}_i$—the radius vector connecting the centers of mass 1 and 2, and $\vec{\xi}_i$—the collection of the remaining "internal coordinates" ; second, the set f: $\mathbf{R}_f, \mathbf{r}_f, \vec{\xi}_f$, constructed analogously to the set i with the interchange $1 \leftrightarrow 3$. The total mass of the system is $M = m_1+m_2+m_3$. To the motion in the coordinates $\mathbf{R}_i$ and $\mathbf{R}_f$ we assign the reduced masses, respectively, $M_i = m_3(m_1+m_2)/M$ and $M_f = m_1(m_2+m_3)/M$; to the motion in the coordinates $\mathbf{r}_i$ and $\mathbf{r}_f$, the reduced masses $m_i = m_1m_2/(m_1+m_2)$ and $m_f = m_2m_3/(m_2+m_3)$. The total Hamiltonian of the system $\mathcal{H}$ can be split into parts in the following two ways:

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

where $\mathcal{K}_\alpha$ is the kinetic-energy operator of the motion in $\mathbf{R}_\alpha$, and V_α is that part of the interaction which tends to zero as $R_\alpha \to \infty$. The asymptotic states (for $R_\alpha \to \infty$) of the problem under consideration, which are eigenfunctions of $(\mathcal{K}_\alpha + h_\alpha)$, are specified by the functions

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

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

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

Thus, an asymptotic state is characterized, in addition to the channel index $\alpha = i, f$, also by the value of the momentum $\mathbf{k}_\alpha$ and the index n, characterizing the quantum numbers of the bound state.

* In the presence of identical particles, the definition of the reaction channels and asymptotic functions is generalized in a trivial way following (1).

Let us now introduce, in the same way as was done, for example, in ([2]), the functions $\psi_{an}(\mathbf{r}_a, \vec{\xi}_a; \mathbf{R}_a)$, which are eigenfunctions of $\mathcal{H}_a$ depending on $\mathbf{R}_a$ as on a parameter:

$$\mathcal{H}_a \psi_{an}(\mathbf{r}_a, \vec{\xi}_a; \mathbf{R}_a) = \mathcal{E}_{an}(\mathbf{R}_a) \psi_{an}(\mathbf{r}_a, \vec{\xi}_a; \mathbf{R}_a),$$

$$\psi_{an}(\mathbf{r}_a, \vec{\xi}_a; \mathbf{R}_a) \underset{R_a \to \infty}{\longrightarrow} \varphi_{an}(\mathbf{r}_a, \vec{\xi}_a), \qquad \mathcal{E}_{an}(\mathbf{R}_a) \to \mathcal{E}_{an}, \tag{5}$$

$$(\psi_{an'}, \psi_{an})_a \equiv \int \psi_{an'} \psi_{an}\, (d\mathbf{r}_a)(d\vec{\xi}_a) = \delta_{n'n}.$$

Let us introduce the projection operators Π_{an} in the space $\mathbf{r}_a, \vec{\xi}_a$:

$$\Pi_{an}\Psi = \psi_{an}(\psi_{an}, \Psi)_a.$$

From Π_{an} we in turn construct the operators

$$\Pi_a = \sum_{n=0}^{n_{\max}} \Pi_{an},$$

where the summation over n runs from the ground state $n = 0$ to some finite $n_{\max}$, which in each specific problem is determined by the condition introduced below*. We also introduce the operators $\Sigma_a = 1 - \Pi_a$, with

$$\Pi_a \Sigma_a = \Sigma_a \Pi_a = 0, \qquad \Pi_a \mathcal{H} \Sigma_a = \Pi_a \mathcal{K}_a \Sigma_a \quad (a = i, f). \tag{6}$$

We shall denote by $\Psi^{\pm}_{ank}$ the complete solutions of the stationary scattering problem, constructed on Φ_{ank}, with incoming and outgoing waves, respectively ([3]). To determine elastic scattering, as well as scattering with transitions between discrete states $n \leq n_{\max}$ in one reaction channel, it is sufficient to construct

$$\widetilde{\Psi}^{\pm}_{ank} = \Pi_a \Psi^{\pm}_{ank} (n \leq n_{\max}).$$

The functions $\widetilde{\Psi}^{\pm}_{ank}$ obey the equation (everywhere $\varepsilon \to +0$):

$$\Pi_a \left[(H - E) + \mathcal{K}_a \Sigma_a \frac{1}{\Sigma_a (E - H \pm i\varepsilon) \Sigma_a} \Sigma_a \mathcal{K}_a \right] \Pi_a \widetilde{\Psi}^{\pm}_{ank} \equiv (H - E + \Delta^{\pm}_a) \widetilde{\Psi}^{\pm}_{ank} = 0; \tag{7}$$

$$\Delta^{\pm}_a = [\Pi_a, \mathcal{K}_a] + [\Pi_a, \mathcal{K}_a] \Sigma_a \frac{1}{\Sigma_a (E \pm i\varepsilon - H) \Sigma_a} \Sigma_a [\mathcal{K}_a, \Pi_a].$$

The introduced functions may be represented in the form

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

where the summation over n' is extended** from $n' = 0$ to $n_{\max}$.

By means of the same operator algebra that was used in ([5]) in deriving the formula for the distorted waves, taking into account the finiteness

* We assume that for $n \leq n_{\max}$ the functions $\mathcal{E}_{an}(\mathbf{R})$ (for the same symmetry of the functions ψ_{an}, which we take into account in the index n) do not cross. In fact, a case of their crossing requiring special consideration is possible ([2]); for point centers $\mathcal{E}_{an}(\mathbf{R})$ actually depends on two arguments: one of the angles specifying $\mathbf{R}$ in spherical coordinates does not enter into $\mathcal{E}_{an}(\mathbf{R})$.

** For $y_{n',\,ank}$ one may write the following system of equations and boundary conditions:

$$[\mathcal{K}_a - (\mathcal{E}_{an}(\mathbf{R}) - \mathcal{E}_{an}) - (E - \mathcal{E}_{an})]\, y^{\pm}_{n,\,ak}(\mathbf{R}_a) = - \sum_{n=0}^{n_{\max}} \{ (\psi_{an}, [\mathcal{K}_a, \psi_{an'}])_a$$

$$- (\psi_{an}, \mathcal{K}_a \Sigma_a \frac{1}{\Sigma_a (E + i\varepsilon - \mathcal{H}) \Sigma_a} \Sigma_a \mathcal{K}_a \psi_{an'})_a \Big\} y_{n',\,ank'}(\mathbf{R}_a),$$

$$y_{n',ank} \underset{R_a\to\infty}{\longrightarrow} \delta_{n'n}\sqrt{k_a/M_a}\,\exp(i\mathbf{k}_a\mathbf{R}_a) + f_{n'n}(\mathbf{k}_a\mathbf{k}'_a)\exp(\pm i|\mathbf{k}'_a|R_a)/R_a,$$

where $k_a'^2$ lies on the energy surface. Finding $y_{a',an}$ is equivalent to, and presents no fundamental difficulties in, solving the problem of potential scattering with a finite discrete number of internal states and a sufficiently rapidly decreasing nonlocal and complex potential.

$(\Phi_{\alpha n'k'},\ \Psi_{\alpha nk})$ for $\alpha' \neq \alpha$, we obtain the expression for the rearrangement T-matrix

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

where the asterisk denotes Hermitian conjugation. An alternative expression is obtained by replacing in (8) the first term in square brackets by $-(\Delta^-_{\alpha'})^*$. Formula (8) can be rewritten in the form

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

where

$$\begin{aligned}\tilde{u}_{\alpha'\alpha} = &-\Pi_{\alpha'}\left(1+[\Pi_{\alpha'},\mathcal{K}_{\alpha'}]\Sigma_{\alpha'}\frac{1}{\Sigma_{\alpha'}(E+i\varepsilon-\mathcal{H})\Sigma_{\alpha'}}\Sigma_{\alpha'}\right)[\Pi_\alpha,\mathcal{K}_\alpha]\\ &\times\left(1+\Sigma_\alpha\frac{1}{\Sigma_\alpha(E+i\varepsilon-\mathcal{H})\Sigma_\alpha}\Sigma_\alpha[\mathcal{K}_\alpha,\Pi_\alpha]\right)\Pi_\alpha.\end{aligned} \tag{10}$$

The principal role in (10) is played by the quantities
$\mathcal{G}(\Sigma_\alpha) = \Sigma_\alpha[\Sigma_\alpha(E+i\varepsilon-\mathcal{H})\Sigma_\alpha]^{-1}\Sigma_\alpha$. For them one may write the integral equation

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

In this case

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

where the sum over n is taken over the whole spectrum of $\mathcal{H}_\alpha$ for $n > n_{\max}$.

We shall assume that a choice of $n_{\max}$ is possible such that $E - \mathcal{E}_{\alpha n}(\mathbf{R}) = k_{\alpha 0}^2/2M_\alpha - (\mathcal{E}_{\alpha n}(\mathbf{R}) - \mathcal{E}_{\alpha 0}) \ll 0$ for $n > n_{\max}$ and for all values of $\mathbf{R}_\alpha$ entering the expression for the T-matrix.

Substitution of the solutions of (11) by means of iterations into (9), (10) will, at low energies, give an expansion for the rearrangement T-matrix in the parameter

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

which passes, when the motion described by (8) can still be regarded as quasiclassical, into
$\max \hbar k_{\alpha 0}/2M\lambda|\mathcal{E}_{\alpha n}(\mathbf{R}) - \mathcal{E}_{\alpha 0}|$ $(n > n_{\max})$, where λ is the characteristic distance over which the influence of the third particle on the bound state of the other two particles in channels i and f decreases. It is not difficult to see that the latter parameter is equivalent to the parameter entering Massey' s criterion [6] for excitation of levels with $n > n_{\max}$. In this case the first term of the indicated expansion, T^0, is in the general case equal to

$$T^0_{\alpha' n' k', \alpha n k} = -(\widetilde{\Psi}^-_{\alpha' n' k'}[\Pi_\alpha, \mathcal{K}_\alpha]\widetilde{\Psi}^+_{\alpha n k}). \tag{14}$$

The first nonvanishing terms of such an expansion are in fact used in many approximate methods of calculation; in particular, they are used in various areas under the names of almost adiabatic methods, the quasimolecule method, the transition-complex method, and almost (or exactly) resonant methods (in charge exchange) [6]. In the latter case it is sometimes considered possible to regard, approximately, the functions from different channels $\psi_{\alpha' n'}$ and $\psi_{\alpha n}$ in the reaction region as eigenfunctions of a single approximate Hamiltonian (for example, when particle 2 is much lighter than the others). In this case the first term of the expansion (14) vanishes. This circumstance

can be understood, since the formation of collision complexes from heavy particles (Breit–Wigner resonances), which depends sharply on the kinetic energy and corresponds to the phase passing through $k\pi/2$ (classical delay), can be contained (for "smooth" elastic scattering) only in the higher terms of the T-matrix with energy-dependent denominators.

It should be especially emphasized here that the kernel of the integral equation (11) is not, as is easy to verify, completely continuous ([7]). Therefore the use of a simple iterative expansion without rearrangement of the kernel may lead to qualitatively erroneous conclusions. Evidently, precisely this circumstance is the reason for the rapid course of some reactions in contradiction to the Massey criterion ([7]).

Another very important feature of the expressions obtained for the rearrangement matrix is that expressions of the form (14) have sharp maxima simultaneously 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 associated with any collision complexes and correspond to wave resonances not of the Breit–Wigner type. These resonances correspond to an optimal correlation (in atom–molecular collisions, quasiclassical) of the motions along the coordinates $\mathbf{R}_i$ and $\mathbf{R}_f$ with internal, essentially quantum, motions. Consequences of the existence of such a correlation in the specific case of chemical reactions are considered in the authors' work ([9]).

In conclusion we note that the treatment presented makes it possible to express the probability of reactions in terms of the characteristics of asymptotic states and elastic scattering without explicitly specifying the interaction potentials.

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Note: Figure translations are in progress. See original paper for figures.