Arrangement-channel approach to reactive systems: Generalizations with new insight

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Recently one of the authors presented the first three-dimensional quantum-mechanical calculations for the \( \text{H} + \text{H}_2 \) system using the Baer-Kouri-Levin-Tobocman (BKLT) equations. The set of equations consists of three coupled Lippmann-Schwinger equations—one for each arrangement—which are coupled via a matrix \( W \) with elements \( W_{\lambda \lambda'} \), which fulfill for each arrangement \( \lambda' \) the condition

\[
\sum_{\lambda'} W_{\lambda \lambda'} = 1, \quad (1)
\]

but is otherwise not restricted. The new idea that led ultimately to a successful three-dimensional application of these equations is to discard the assumption that the \( W \)-matrix elements are constants and to assume them to be functions of the internal coordinates of the three-particle system. In our particular treatment we assumed them to depend on the three orientation angles \( \gamma' = \cos^{-1}(\vec{R}_{\alpha} \cdot \vec{r}_{\lambda}) \); in the present communication we discuss two other possibilities for functional forms of the \( W_{\lambda \lambda'} \): one is now used under the name Fock coupling scheme and the other leads to a new set of integral (and differential) equations with the attractive feature of being symmetric.

In order to obtain the Fock scheme from the BKLT equations we start with the BKLT equation for the \( R \)-matrix elements:

\[
R_{\lambda \lambda'} = V_{\lambda} W_{\lambda \lambda'} + V_{\lambda'} \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} R_{\lambda'' \lambda'}, \quad (2)
\]

where \( V_{\lambda} \) is the perturbation potential \( (H = H_{\text{at}} + V_{\lambda}) \) and \( G_{\lambda''} \) is the distorted wave principal value Green function. Summing over \( \lambda' \) yields

\[
\sum_{\lambda''} R_{\lambda \lambda''} = \sum_{\lambda''} V_{\lambda''} W_{\lambda'' \lambda} + \sum_{\lambda''} \left( \sum_{\lambda'} W_{\lambda \lambda'} \right) G_{\lambda''} R_{\lambda'' \lambda}, \quad (3)
\]

Now if the \( W \)-matrix elements are chosen in such a way that

\[
\sum_{\lambda'} V_{\lambda'} W_{\lambda \lambda'} = V_{\lambda}, \quad (4)
\]

[this choice is compatible with Eq. (1)], then

\[
\sum_{\lambda''} R_{\lambda \lambda''} = V_{\lambda} + \sum_{\lambda'} V_{\lambda'} G_{\lambda'} R_{\lambda \lambda'} \quad (5)
\]

which can also be written as

\[
R_{\alpha \lambda} = V_{\lambda} + \sum_{\lambda'} V_{\lambda'} G_{\lambda'} R_{\lambda \lambda'}, \quad (5')
\]

Here \( \alpha \) may be any of the three channel numbers. Defining now the amplitude density function as

\[
\xi_{\lambda} = R_{\alpha \lambda} \phi_{\lambda}, \quad (6)
\]

(where \( \phi_{\lambda} \) is the solution of the unperturbed Hamiltonian) and multiplying Eq. (5') by \( \phi_{\lambda} \) leads to

\[
\xi_{\lambda}^{2} = V_{\lambda} \phi_{\lambda} + \sum_{\lambda'} V_{\lambda'} G_{\lambda'} \xi_{\lambda'} - \sum_{\lambda' + \alpha} \xi_{\lambda'}, \quad (7)
\]

which is the equation employed in the Fock coupling scheme.

To obtain out of Eq. (7) three independent equations for the three unknown functions \( \xi_{\lambda}^{2} \); \( \alpha = \lambda, \nu, k \), one expands each of the \( \xi_{\lambda}^{2} \) in a \( L^{2} \) basis set within its own arrangement channel. No ambiguity can arise (as long as the continuum is not included) because each function is characterized by its own coordinates, namely \( (R_{\alpha}, r_{\alpha}) \).

In order to obtain a better understanding of the second representation we write Eq. (2) in a matrix form:

\[
R = \tilde{V} + \tilde{V}G, \quad \tilde{V} = VW, \quad (8)
\]

where \( \tilde{V} \) is the generalized potential matrix defined as

\[
\tilde{V} = WV. \quad (9)
\]

The choice for \( W \) will now be done in such a way that \( \tilde{V} \) is symmetric:

\[
\tilde{V}_{\lambda \lambda'} = \tilde{V}_{\lambda' \lambda} \Rightarrow V_{\lambda} W_{\lambda \lambda'} = V_{\lambda'} W_{\lambda \lambda'}, \quad (10)
\]

Equation (1) together with Eq. (10) yields six algebraic equations for the nine unknown \( W \)-matrix elements. For the sake of convenience we assume the three diagonal elements to be zero. Solving the six equations leads to

\[
W_{\lambda \lambda'} = \frac{V_{\lambda} + V_{\lambda'} - V_{\nu}}{2V_{\lambda}}, \quad \lambda \neq \lambda', \lambda' \neq \nu, \nu \neq \lambda, \quad (11)
\]

which by substituting in Eq. (10) yields for the \( \tilde{V} \) elements the symmetric form

\[
\tilde{V}_{\lambda \lambda'} = \frac{1}{2} (V_{\lambda} + V_{\lambda'}, - V_{\nu}); \quad \lambda \neq \lambda', \lambda' \neq \nu, \nu \neq \lambda. \quad (12)
\]

The advantage in having a symmetric \( V \) matrix may not be obvious from the integral equation form given in Eq. (8), because in front of \( R \) there is \( \tilde{V}G \) and not \( \tilde{V}G \). If the Schrödinger representation is used instead, the advantage becomes more apparent; Defining \( \Psi \) as a sum of the three arrangement channel wave functions, i.e.:

\[
\Psi = \sum_{\lambda} \psi_{\lambda}, \quad (13)
\]

it can be shown that the \( \psi_{\lambda} \)'s fulfill the equation:

\[
(E - H_{\text{at}}) \psi_{\lambda} = \sum_{\lambda} W_{\lambda \lambda'} V_{\lambda'} \psi_{\lambda'} - \tilde{V}_{\lambda \lambda'} \psi_{\lambda'}, \quad (14)
\]

where \( H_{\text{at}} \) is the unperturbed Hamiltonian related to the \( \lambda \) arrangement. Equation (14) can be written in a matrix form:

\[
(E I - H_{0}) \psi - \tilde{V} \psi = 0, \quad (15)
\]

where \( H_{0} \) is a diagonal matrix with the operators \( H_{\text{at}}, \alpha = \lambda, \nu, k \) in the diagonal, \( I \) is the unity matrix, \( \psi \) is the
solution vector, and $\tilde{V}$ is a symmetric potential matrix.

The above choice of $W$ will lead to a set of integral (or differential) equations which can be expected to be more stable numerically than other equations because a symmetric potential matrix guarantees a Hermitian $S$ matrix. During the last few years we were able to solve the BKL equations for various exchange problems (and as mentioned earlier, also for the $H + H_2$ reaction in three dimensions); however, we also realized that the different choices of $W$ led to a relatively slow convergence process. It is our hope that this new set of equations presented here will converge significantly faster.

A more detailed study of this new representation will be given elsewhere.$^{10}$

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Secondary critical points in the supercritical region of a van der Waals fluid

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The well known van der Waals equation of state $(P + a/\tilde{V}^2)(\tilde{V} - b) = RT$ provides a semiquantitative$^5$ representation of the main features of PVT behavior near the liquid–vapor critical point. Here we examine the supercritical isotherms of a van der Waals fluid and note several characteristics that may be significant in real systems.

Figure 1 shows eight reduced isotherms for the fluid in its critical region. The liquid–vapor coexistence curve (E) is sketched in with a dashed line. Point C represents the end of normal vaporization–condensation behavior. At temperatures not far above $T_c$, the fluid remains very nonideal; in fact pseudocritical condensation can occur in a long vessel, particularly if it happens to be undergoing high acceleration. The persistence of a region of very small slope in the isotherms (e.g., 5 in the figure) can, in a quiescent fluid, create a large density difference between the end regions of the vessel, and a steep gradient in the density in some intermediate region—a diffuse and easily destabilized “liquid–vapor interface.” In approximately the same transition region one would observe maximal light scattering from the fluid and a minimum in the velocity of sound.$^1$

As the temperature is raised, the pseudocritical or sigmoid density distribution eventually disappears, because there no longer is a point of minimum slope in the isotherms; they are concave upward at all $\tilde{V}$. A characteristic temperature for this can be identified. It is found by differentiating the equation of state and obtaining the equation giving the loci of the points of inflection $[(\partial^2P/\partial\tilde{V}^2)_{T} = 0]$ in isotherms. The equation is

$$RT/3a = (\tilde{V} - b)^3/\tilde{V}^4. \quad (1)$$

At sufficiently low temperatures, Eq. (1) has two real roots. The one at smaller $\tilde{V}$ is at the point of the minimum in $(\partial^2P/\partial\tilde{V}^2)_{T}$, while the root at larger $\tilde{V}$ is at the maximum. The locus of the roots at temperatures above $T_c$ is shown as curve F in the figure.$^6$ The roots converge to a single value at point m, which thus is a critical point: there are no solutions at temperatures above $T_m$; i.e., there are no extrema in the slopes of isotherms above this temperature. Differentiation of Eq. (1) yields this maximum temperature and the associated $\tilde{V}_m$ and $P_m$:

$$\tilde{V}_m = 4b; \quad V^*_m = \tilde{V}_m/\tilde{V}_c = 1.333,$$

$$P_m = 11a/256b; \quad P^*_m = P_m/P_c = 1.160,$$

$$T_m = 81a/256R_b; \quad T^*_m = T_m/T_c = 1.068.$$

The region delineated by curve F extends well above the liquid–vapor critical temperature. $T_m$ for CO$_2$ lies some 21 K above $T_c$. For heptane, $T_m - T_c \approx 35$ K.

The compressibility coefficient $\beta = (1/\tilde{V})(\partial \tilde{V}/\partial P)_T$ also exhibits critical behavior, in that it has a maximum and a minimum on every supercritical isotherm up to a maximum temperature $T_{m*}$ at which the two extrema converge, and beyond which there are no extrema. This point is identified as $\beta_m$ in the figure, and the locus of extrema is given by the intersections of curve G with the isotherms.

The governing equation, analogous to Eq. (1), is

$$RT/4a = (\tilde{V} - b)^3/\tilde{V}^4(\tilde{V} + b) \quad (2)$$

which has two real roots for all $T$ below $T_{m*}$. (This time the roots at the smaller $\tilde{V}$'s are positions of maxima, and those at larger $\tilde{V}$ of minima.)