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On Expansion of Exchange Kernels for Reactive Scattering

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Abstract

Two methods of treating the exchange kernel appearing in Miller's formulation of reactive scattering are investigated, with the most promising being an improvement of the separable expansion used previously. On the basis of results for the collinear H + H_2 reaction, it appears that calculations within this formalism can be tractable for more general bimolecular reactions.

I. Introduction

In a recent paper by Garrett and Miller,[1] the general formulation of reactive scattering previously described by Miller[2] has been applied to the $H + H_2$ collinear reaction. Such a formalism, which avoids the use of methods which must be explicitly matched to each individual problem, has been shown to generate reaction probabilities with an accuracy comparable to that obtained by the more specialized methods.[3] It was noted, however, that the calculation has a somewhat disquieting feature in that an expansion made for the non-separable exchange interaction term necessitates the use of a large number of expansion functions in order to adequately describe the direct exchange effect. Thus one may ask if there is a better but yet still convenient way of handling such a non-separable exchange term. Once such an improved characterization has been obtained, the application of this general reactive scattering formalism to other bimolecular collisions should become computationally tractable and thereby should provide an attractive method for studying more chemically interesting processes.

Two approaches to the improvement of the exchange kernel description are presented in detail in Section III. The first involves an attempt to solve directly the integro-differential equations arising from the theory by an iterative procedure. However, for physically realistic exchange terms it appears that the magnitude of the kernel is sufficiently large that the iteration scheme will not converge in its present form. The second approach concerns an alternate method for constructing a separable expansion of the exchange kernel which allows more knowledge of the interaction to be built into the description. As indicated below, we shall show that this improved separable approximation does indeed do a very good job of reducing the number of basis functions required for an adequate characterization of the rearrangement process.

II. Review of the Theory

Inasmuch as the details of Miller's formulation of the reactive scattering problem are given elsewhere,[1,2] we will merely note the important features of the formalism here. For a collinear reaction of the general form A + BC → AB + C for which the collision energy is such that only the ground vibrational states of reactants and products are open, one writes the wavefunction describing scattering from the initial channel α_0(α_0 = a or c) as

$$\Psi_{\alpha_0}(r,R) = \phi_a(r_a)f_{a\leftarrow\alpha_0}(R_a) + \phi_c(r_c)f_{c\leftarrow\alpha_0}(R_c) + \sum_n C_n\chi_n(r,R)$$

where a(A+BC) and c(AB+C) label the two possible asymptotic arrangements for which (r_a,R_a) and (r_c,R_c) respectively are the appropriate Jacobi coordinates, only two of the four coordinates being independent. Initially one presumes knowledge both of the wavefunctions which characterize the asymptotic diatomic vibrational states, $\phi_a(r_a)$ and $\phi_c(r_c)$, and also of a finite set of square-integrable functions $\{\chi_n\}$ which describe the effect of the energetically closed channels. Then, by application of a variational principle, one determines the expansion coefficients $\{C_n\}$ and thereby the set of coupled equations to be solved for the unknown radial functions, $f_{a\leftarrow\alpha_0}(R_a)$ and $f_{c\leftarrow\alpha_0}(R_c)$.

If, however, the discussion is specialized to the H + H_2 exchange reaction, one may take advantage of the symmetry of the resulting equations and construct a set of decoupled equations for the functions $f_+(R)$ and $f_-(R)$ defined by

$$f_\pm(R) = f_{a\leftarrow\alpha_0}(R) \pm f_{c\leftarrow\alpha_0}(R) \qquad .$$

Thus, by addition and subtraction of the coupled equations, the following independent integro-differential equations are obtained:

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R)-E_0]\ f_\pm(R) \pm \int dR'\ V_{ex}(R,R')\ f_\pm(R')$$

$$+ 2\sum_{n,m}^{\pm} A_n(R)(\underset{\approx}{M}^{-1})\langle A_m|f_\pm\rangle = 0 \qquad (2.1)$$

where

$$V_0(R) = \int dr\ \phi_0(r)^*[V-v_0(r)]\ \phi_0(r)$$

$$V_{ex}(R,R') = \frac{\partial r(R,R')}{\partial R}\ [-\frac{\hbar^2}{2\mu}\ \frac{d^2}{dR'^2} + V-v_0(r')-E_0]$$

$$\cdot\ \phi_0[r(R,R')]\ \phi_0[r'(R,R')]$$

$$M_{n,m} = \langle\chi_n|E-H|\chi_m\rangle$$

$$A_n(R) = \int dr\ \phi_0(r)^*(H-E)\chi_n(r,R)$$

$$\phi_0(R) = \phi_a(R) = \phi_c(R)$$

$$E_0 = E - \varepsilon_0 \quad .$$

In the above equations H is the total Hamiltonian, V is the total potential energy, $v_0(r)$ is the asymptotic ground vibrational potential function for H_2, and ε_0 is the vibrational eigenvalue corresponding to $\phi_0(r)$. Since the correlation functions $\{\chi_n\}$ are chosen to have a definite parity upon the exchange $(r_a,R_a) \leftrightarrow (r_c,R_c)$ and furthermore since the matrix M does not contain matrix elements which connect states of differing parity, the summation in Eq. (2.1) retains only the correlation terms of + or - parity.

Inasmuch as the term which describes the closed-channel effects is explicitly separable and hence is inherently easier to handle, we shall restrict our discussion which follows to a consideration of the nature of the open-channel exchange effect. Thus, instead of examing Eq. (2.1) as a whole, our study is based on the equation

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R)-E_0]\ f_\pm(R) = \mp\int dR'\ V_{ex}(R,R')\ f_\pm(R') \qquad (2.2)$$

which includes only the energetically open channels.

III. Treatment of the Exchange Kernel

a. Iterative Solution

As has been previously indicated,[1] there is an obvious analogy between these scattering equations and the conventional Hartree-Fock expansions of electronic structure theory. One is tempted, therefore, to try to solve the equations via an iteration scheme analogous to an SCF calculation:

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R)-E_0]\; f_\pm^{(n)}(R) = \mp\int dR'\; V_{ex}(R,R')\; f_\pm^{(n-1)}(R') \qquad (3.1)$$

where n counts the iterations.

If $f_0(R)$ is the regular solution of the homogeneous differential equation, i.e.,

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R)-E_0]\; f_0(R) = 0 \qquad (3.2)$$

then the iterative process is begun by taking $f_\pm^{(0)}(R) \equiv f_0(R)$, substituting the zeroth order solution into the right hand side of Eq. (3.1), integrating this inhomogeneous equation to determine $f_\pm^{(1)}(R)$, then repeating the cycle until $f_\pm^{(n)}(R) = f_\pm^{(n-1)}(R)$ to the accuracy desired. Note also that such an operation is equivalent to summing a Born series;[4] for example, a single iteration yields the solution obtained via the usual distorted-wave Born approximation.

The difficult with such an approach lies, of course, in the convergence properties of Eq. (3.1). To get an idea of the conditions under which a solution may be obtained by iteration, consider a simple separable approximation to the exchange kernel,

$$V_{ex}(R,R') = A\, g(R)\, g(R') \quad ,$$

where g(R) might, for example, be a gaussian centered about the maximum of V_{ex}. For this case, Eq. (2.2) then reduces to

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R) - E_0]\, f_\pm(R) = \mp A\, g(R)\, \langle g|f_\pm\rangle \qquad (3.3)$$

which is known to be solvable in a closed form,

$$f_\pm(R) = f_0(R) \pm G_0 g \cdot A\langle g|f_0\rangle (1 \mp A\langle g|G_0|g\rangle)^{-1} \quad ,$$

where G_0 is the Green's function corresponding to Eq. (3.2). Once the solution is in this form, one can identify the convergence criterion by noting that the second term on the right has the form of the sum of a geometric series, for which the convergence properties are well known.[5] Thus one sees that an iterative solution will be obtainable if and only if

$$|A\langle g|G_0|g\rangle| < 1 \quad . \qquad (3.4)$$

Unfortunately, our calculations have shown that Eq. (3.4) will not generally be satisfied for realistic fits of the separable form to the actual $V_{ex}(R,R')$ at collision energies for which the reaction probabilities are non-negligible. Consequently, one finds that inclusion of the rearrangement effects produces a significant additional phase shift, making $f_0(R)$ a poor approximation to $f_\pm(R)$. The higher terms in the Born series will, therefore, make a significant contribution to the scattering, so that a distorted-wave Born approximation is clearly insufficient.

One also notices that the analogy between this development and Hartree-Fock theory is not as close as might be hoped. In practice the exchange kernel, although manifestly nonlocal, is confined to a relatively small region of space ($R,R' = [1.,5.]$ bohr) and as such does not produce the average potential field which is characteristic of electron exchange. Therefore one should not be too surprised that an SCF-like approach to equations describing molecular rearrangement is not particularly successful.

b. Separable Expansion of V_{ex}

Garrett and Miller,[1] in the initial complete application of the exchange kernel formalism, made a separable approximation to V_{ex}, namely

$$V_{ex}(R,R') = \sum_{i,j} u_i(R) \langle u_i|V_{ex}|u_j\rangle u_j(R') \quad , \qquad (3.5)$$

where $\{u_i\}$ is a convenient basis set. Since their calculation was converged with respect to an increase in the number of basis functions, Eq. (3.5) represents an essentially exact treatment of the direct exchange contribution. In addition, the use of a separable expansion greatly facilitates computation in that all of the inhomogeneous terms in Eq. (2.1) are then separable. Consequently one can obtain a solution for $f_{\pm}(R)$ in a closed form. However, as mentioned previously, this "outer" expansion of the kernel requires that a large number of functions be included if convergence is to be achieved, and hence this particular approach would likely prove to be unwieldy for systems larger than H + H_2.

In order to make these calculations more generally applicable, we have investigated a second separable approximation, an "inner" expansion defined by

$$V_{ex}(R,R') = \langle R|V_{ex}\, V_{ex}^{-1}\, V_{ex}|R'\rangle$$

$$= \sum_{i,j} \langle R|V_{ex}|u_i\rangle(\langle u_i|V_{ex}|u_j\rangle)^{-1}\langle u_j|V_{ex}|R'\rangle \qquad (3.6)$$

where $(\langle u_i|V_{ex}|u_j\rangle)^{-1}$ denotes the (i,j) matrix element of the matrix inverse of the matrix $\langle u_i|V_{ex}|u_j\rangle$. Note that now the epansion vectors are $\{V_{ex}u_i\}$ rather than $\{u_i\}$, and accordingly more knowledge of the exchange is built directly into the development.

To see the consequences of improving the approximation for V_{ex}, consider another very simple model for the exchange,

$$V_{ex}(R,R') = A\delta(R-R_0)\ \delta(R'-R_0) \quad ,$$

a model which is localized (in the extreme) at $R = R' = R_0$; note that the actual kernel for $H + H_2$ in reference 1 is qualitatively of this form. Applying Eq. (3.5) one obtains the outer expansion,

$$V_{ex}(R,R') = A \sum_{i,j} u_i(R)\ u_i(R_0)\ u_j(R')\ u_j(R_0) \quad .$$

On the other hand, using the inner expansion, Eq. (3.6),

$$V_{ex}(R,R') = \sum_{i,j} \frac{A^2\delta(R-R_0)\ \delta(R'-R_0)\ u_i(R_0)\ u_j(R_0)}{A\ u_i(R_0)\ u_j(R_0)}$$

$$= A\delta(R-R_0)\ \delta(R'-R_0) \quad .$$

identically, regardless of the form taken for $\{u_i\}$ or of the number of functions used. Clearly, unless a rather large number of expansion functions are retained, these two expressions will differ significantly. One is therefore encouraged that this inner expansion may substantially improve the characterization of the kernel and in doing so decrease the size of the basis set required for an accurate solution.

IV. Results and Discussion

Our calculations of the H + H_2 collinear reaction probability were performed on the Porter-Karplus[6] potential surface at a collision energy of 0.4898 eV. Except for the way in which V_{ex} was handled, there was little difference between these computations and those previously reported,[1] although we have restricted our present study to the direct exchange contribution since the indirect exchange via the closed channels already seemed well characterized.

In order to obtain the best separable description of V_{ex} while at the same time minimizing the number of basis functions needed in Eq. (3.6), a search was made for the optimum choice of parameters for the $\{u_i\}$. These functions, taken to be harmonic oscillator wavefunctions,[7] contain two free parameters—the point about which the functions are centered, R_0, and a quantity related inversely to the "width" of the functions, β. The results of this search are shown in Table 1, where we list the open-channel reaction probability for various values of β^2; in all cases R_0 was chosen to be the point at which the exchange kernel has a maximum. It is evident that the number of functions required for a converged expansion is strongly dependent upon the choice for β. In contrast, calculations using the outer expansion show convergence which is virtually independent of the function width. This difference in the behavior of the two descriptions suggests that whereas the outer expansion is sufficiently poor that many basis functions must be included regardless of the details of the functional forms, the inner expansion, by providing more flexibility in fitting a specific form of the exchange kernel, requires that the basis functions be "tuned" in order that the fit be optimized. Thus, for large values of β, one is obliged to use many functions just to span the coordinate space over which the rearrangement is most likely to occur simply because the spanning functions are themselves too localized. On the other hand, for very small β, the functions become so spread out that they have a substantial amplitude in the region of the respulsive wall of the potential, a region which is poorly described in general. Therefore one expects the optimum choice for β to appear in an intermediate region, this expectation being borne out by the tabulated results.

The primary point of this paper, as seen in Table 1, is that the inner expansion provides a much more efficient representation of the exchange kernel. For the optimum choice of β, for example, a converged reaction probability accurate to three significant figures is obtained with only 8 basis functions via the inner expansion, whereas 25 basis functions are required to achieve this accuracy with the outer expansion.

Overall this improved expansion of the exchange kernel provides a significant reduction in the magnitude of the computational problem which is associated with Miller's reactive scattering formalism. Such a reduction, hopefully, has made the extension of this method to higher dimensions or to more chemically interesting collision partners much more feasible.

Acknowledgments

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Table 1. Open-channel reaction probabilities for collinear H + H_2

Number of	Width parameter, β^2						
expansion functions	24.0	20.0	16.0	12.0	7.0	4.0	1.0
2	.0001	.0000	.0008	.0130	.0938	.1736	.0006
4	.0082	.0441	.1407	.7078	.1294	.1139	.1134
6	.2613	.1501	.1163	.1064	.1082	.1124	.1138
8	.1055	.1026	.1029	.1043	.1147	.1137	.1154
10	.1010	.1016	.0958	.1159	.1137	.1137	.1171
12	.0966	.1365	.1149	.1138	.1137	.1137	.1120
14	.1176	.1143	.1138	.1137	.1137	.1144	.0790
16	.1140	.1137	.1137	.1140	.1137	.1137	.1266
18	.1137	.1137	.1137	.1137	.1137	.1141	.0818
20	.1137	.1137	.1137	.1137	.1137	.1139	.1033

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