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Garrett, Bruce G.

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October 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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LBL-6971

Quantum Mechanical Reactive Scattering via Exchange Kernels: Application to the Collinear $H + H_2$ Reaction*

Bruce C. Garrett and William H. Miller‡

Department of Chemistry and Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

ABSTRACT

A formulation of quantum mechanical reactive scattering given by Miller is applied to the collinear $H + H_2$ reaction. The approach is the direct analog to the Hartree-Fock method of electronic structure theory, and it obviates the need for specialized (e.g., "natural" collision) coordinates. The rearrangement process takes place via an explicit exchange interaction (cf. electron exchange in Hartree-Fock theory), and closed channels are incorporated via a square-integrable set of correlation functions. Agreement with results obtained by others using other methods is excellent, showing this approach to quantum mechanical reactive scattering to be a viable one.

Work performed under the auspices of the U. S. Department of Energy.

I. Introduction

In recent years much progress has been made in the quantum mechanical description of molecular collisions in which rearrangement channels are open.[1-4] The major complication in treating rearrangement collisions arises from the fact that coordinates descriptive of the asymptotic reactant arrangement differ from those describing the asymptotic product arrangements.

One method of approaching this problem is to use a coordinate system which goes smoothly from reactants to products--i.e., natural collision coordinates.[1] Another method is to solve the coupled channel equations in each arrangement and match the solutions in the interaction region.[2] Both of these methods have the undesireable characteristic that they must be tailored to the specific problem at hand.

A more general formulation of reactive scattering was given a number of years ago by Miller.[5] Here the wavefunction is expanded in the internal states of all arrangements, and the coupled channel equations are obtained from a variational principle. This approach is the direct analog of the Hartree-Fock expansion familiar in electronic structure theory, and it obviates the need for any special (e.g., natural collision) coordinates. The price paid is that the coupled equations contain a non-local exchange interaction analogous to electron exchange in Hartree-Fock theory.

The only application of this approach to date has been Wolken and Karplus'[6] three dimensional calculation for the H + H_2 reaction. This work, however, included only the ground vibrational state of H_2 in the coupled channel expansion and was thus not fully converged with respect to the expansion in internal states.

In this paper we describe a practical method of dealing with the non-local exchange interaction and present the results of calculations for the collinear H + H_2 reaction. Agreement with results obtained by other workers using other approaches is excellent.

In addition to dealing directly with the non-local exchange interaction, the other novel feature in this approach[5] is that the effect of energetically closed channels is included via a square-integrable set of "correlation functions". With regard to this expansion we observe the variational property of this method, namely that the scattering parameters converge monotonically as the set of correlation functions is enlarged.

Section II summarizes the theory, specialized for the collinear H + H_2 reaction. Results are presented and discussed in Section III.

II. Summary of the Theory

Here we summarize the reactive scattering formalism of Miller,[5] specialized to the collinear A + BC → AB + C reaction. For the collinear reaction only two asymptotic arrangements are possible, a(A + BC) and c(AB + C), for which the coordinates are (r_a, R_a) and (r_c, R_c), respectively; cf. Figure 1. For arrangement a, for example, r_a is the diatomic separation (the distance between B and C), and R_a is the translation coordinate (the distance from A to the center of mass of BC); r_c and R_c are defined similarly for arrangement c.

For translational energies less than ∿ 0.5 eV the ground vibrational state of H_2 is the only open channel. To simplify the formulae we thus assume that only the ground vibrational state of BC and AB are open. If $\phi_a(r_a)$ and $\phi_c(r_c)$ are the vibrational wavefunctions for these states, then the expansion of the wavefunction is

$$\Psi_{\alpha_0}(r,R) = \phi_a(r_a)\, f_{a\leftarrow\alpha_0}(R_a) + \phi_c(r_c)\, f_{c\leftarrow\alpha_0}(R_c) + \sum_n c_n \chi_n(r,R) \quad , \tag{2.1}$$

where $\{\chi_n\}$ is a set of square-integrable "correlation functions" introduced to take account of closed channels. The index α_0 (= a or c) denotes the initial arrangement. The coordinates (r,R) can be either (r_a,R_a) or (r_c,R_c) since only two of these four coordinates (r_a,R_a,r_c,R_c) are independent. For H + H_2, for example, one has

$$r_c = R_a - \frac{1}{2} r_a$$

$$R_c = \frac{1}{2} R_a + \frac{3}{4} r_a \quad . \tag{2.2}$$

The radial functions, $f_{a\leftarrow\alpha_0}(R_a)$ and $f_{c\leftarrow\alpha_0}(R_c)$, and the expansion coefficients $\{C_n\}$ in Eq. (2.1) are determined from a variational principle. The two coupled equations for the two radial functions are

$$\left[-\frac{\hbar^2}{2\mu_a} \frac{d^2}{dR_a{}^2} + V_{aa}(R_a) - E_a\right] f_{a\leftarrow\alpha_0}(R_a) + \int_0^\infty dR_c \, V_{ac}(R_a,R_c) f_{c\leftarrow\alpha_0}(R_c)$$

$$+ \sum_{n,m} A_{an}(R_a) (\underset{\approx}{M}^{-1})_{n,m} \left[\langle A_{ma}|f_{a\leftarrow\alpha_0}\rangle + \langle A_{mc}|f_{c\leftarrow\alpha_0}\rangle\right] = 0 \tag{2.3a}$$

and

$$\left[-\frac{\hbar^2}{2\mu_c} \frac{d^2}{dR_c{}^2} + V_{cc}(R_c) - E_c\right] f_{c\leftarrow\alpha_0}(R_c) + \int_0^\infty dR_a \, V_{ca}(R_c,R_a) f_{a\leftarrow\alpha_0}(R_a)$$

$$+ \sum_{n,m} A_{cn}(R_c) (\underset{\approx}{M}^{-1})_{n,m} \left[\langle A_{mc}|f_{c\leftarrow\alpha_0}\rangle + \langle A_{ma}|f_{a\leftarrow\alpha_0}\rangle\right] = 0 \quad . \tag{2.3b}$$

μ_a and μ_c are the translational reduced masses for arrangements a and c, and E_a and E_c are the translational energies,

$$E_\alpha = E - \varepsilon_\alpha \quad ,$$

where E is the total energy and ε_α the vibrational eigenvalue corresponding to the vibrational eigenfunction $\phi_\alpha(r_\alpha)$. The interaction diagonal in the arrangement index is a local potential,

$$V_{\alpha\alpha}(R_\alpha) = \int dr_\alpha \; \phi_\alpha(r_\alpha)^* \; [V - v_\alpha(r_\alpha)]\phi_\alpha(r_\alpha) \quad , \tag{2.4}$$

where V is the total potential energy and $v_\alpha(r_\alpha)$ is the asymptotic vibrational potential function for arrangement α, while the interaction non-diagonal in arrangement indices is a non-local, or exchange interaction, the kernel of which is

$$V_{ac}(R_a,R_c) = \frac{\partial r_a(R_a,R_c)}{\partial R_c} \left[- \frac{\hbar^2}{2\mu_c} \frac{\partial^2}{\partial R_c{}^2} + V - v_c(r_c) - E_c\right]$$

$$\phi_a(r_a(R_a,R_c)) \; \phi_c(r_c(R_a,R_c)) \quad , \tag{2.5}$$

and similarly for $V_{ca}(R_c,R_a)$. In Eq. (2.5) the two translational coordinates R_a and R_c are the independent variables; for the $H + H_2$ case, for example, $r_a(R_a,R_c)$ and $r_c(R_a,R_c)$ are determined by Eq. (2.2),

$$r_a(R_a,R_c) = \frac{4}{3} R_c - \frac{2}{3} R_a$$

$$r_c(R_a,R_c) = \frac{4}{3} R_a - \frac{2}{3} R_c \quad . \tag{2.6}$$

The matrix $\underset{\approx}{M}$ in Eq. (2.3) is

$$M_{n,m} = \langle\chi_n|E-H|\chi_m\rangle \quad , \tag{2.7}$$

where H is the total Hamiltonian, and the function $A_{\alpha n}(R_\alpha)$ is

$$A_{\alpha n}(R_\alpha) = \int dr_\alpha \; \phi_\alpha(r_\alpha)^* \; (H-E)\chi_n(r_\alpha,R_\alpha) \quad . \tag{2.8}$$

For the case of $H + H_2$, to which we now specialize the discussion, the two coupled equations in Eq. (2.3) can be decoupled because of symmetry. In Eq. (2.3b) one interchanges the labels $(r_a,R_a) \leftrightarrow (r_c,R_c)$ and denotes $R = R_a$, $R' = R_c$. The correlation functions are chosen to have a definite parity, + or −, upon the exchange $(r_a,R_a) \leftrightarrow (r_c,R_c)$ (i.e., the interchange of the identical atoms A and C), and because of the identity of particles the matrix M has no matrix elements connecting + and − states. If $f_\pm(R)$ is defined by

$$f_\pm(R) = f_{a\leftarrow\alpha_0}(R) \pm f_{c\leftarrow\alpha_0}(R) \quad , \tag{2.9}$$

adding and subtracting Eqs. (2.3a) and (2.3b) leads to the following uncoupled equations for f_+ and f_-:

$$\begin{aligned} &[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R) - E_0]f_\pm(R) \pm \int dR' \, V_{ex}(R,R')f_\pm(R') \\ &+ 2 \sum_{n,m}^{\pm} A_n(R)(\underset{\approx}{M}^{-1})_{n,m} \langle A_m | f_\pm \rangle = 0 \quad , \end{aligned} \tag{2.10}$$

where

$$V_0(R) \equiv V_{aa}(R)$$

$$V_{ex}(R,R') \equiv V_{ac}(R,R')$$

$$A_n(R) \equiv A_{an}(R)$$

$$E_0 \equiv E_a = E_c \quad .$$

The designation ± on the summation in Eq. (2.10) means that the correlation terms of + or - parity are retained in the summation.

Eq. (2.10) is two uncoupled, one-channel radial equations for f_+ and for f_-, so that the regular solutions have the asymptotic form

$$\lim_{R\to\infty} f_\pm(R) \sim \sin(kR + \delta_\pm) \quad , \tag{2.11}$$

where $k = \sqrt{2\mu E_0/\hbar^2}$ and $\delta_\pm$ is the phase shift which is determined by solving Eq. (2.10). Inverting Eq. (2.9),

$$f_{a\leftarrow\alpha_0}(R) = \frac{1}{2}\,[f_+(R) + f_-(R)] \tag{2.12a}$$

$$f_{c\leftarrow\alpha_0}(R) = \frac{1}{2}\,[f_+(R) - f_-(R)] \quad , \tag{2.2b}$$

one can show that the reactive S-matrix is

$$S_{c,a} = \frac{1}{2i}\,(e^{2i\delta_+} - e^{2i\delta_-}) \quad , \tag{2.13}$$

so that the reaction probability,

$$P_{c,a} = |S_{c,a}|^2 \equiv P_R \quad , \tag{2.14}$$

is given by

$$P_R = \sin^2(\delta_+ - \delta_-) \quad . \tag{2.15}$$

The task, then, is to solve Eq. (2.10) to determine the phase shifts δ_+ and δ_-, the reaction probability then being given by Eq. (2.15).

The terms in Eq. (2.10) which involved the correlation functions $\{\chi_n\}$ are easy to deal with since they have the form of a separable exchange interaction. The nonseparable exchange term, V_{ex}, is intrinsically more difficult to handle. The physical distinction between these two exchange interactions is that the nonseparable exchange V_{ex} is the direct exchange between open channels, while the separable exchange interaction resulting from the correlation functions is the indirect exchange that takes place through closed channels. If the reaction mechanism involves a long-lived collision complex, then this feature is described by the correlation functions.

The principle novel aspect of this paper is that we treat the nonseparable exchange interaction by making a separable expansion of it,

$$V_{ex}(R,R') = \sum_{i,j} u_i(R) \langle u_i | V_{ex} | u_j \rangle u_j(R') \quad , \qquad (2.16)$$

where $\{u_i\}$ is some convenient basis set. For a finite basis set, which is always necessary in practice, Eq. (2.16) is an approximation, but it can be made successively better by including more basis functions. In practice, therefore, one must increase the number of basis functions to insure conversions of this expansion.

With the approximation in Eq. (2.16), both exchange interactions in Eq. (2.10) are separable, and it is well known that a closed form solution of Eq. (2.10) is then possible. Thus the equation has the generic form

$$[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_0(R) - E_0]f(R) + \sum_{i,j} g_i(R)\, A_{i,j}\, \langle g_j|f\rangle = 0 \quad , \tag{2.17}$$

where the functions $\{g_i(R)\}$ and the matrix $A_{i,j}$ are known. If $f_0(R)$ and $f_1(R)$ are the regular and irregular solutions, respectively, to the Schrödinger equation with only the local potential,

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{2R^2} + V_0(R) - E_0\right]\begin{Bmatrix} f_0(R) \\ f_1(R) \end{Bmatrix} = 0 \quad , \tag{2.18}$$

with asymptotic form

$$\lim_{R\to\infty} f_0(R) \sim \sin(kR) + \tan\delta_0 \cos(kR) \tag{2.19a}$$

$$\lim_{R\to\infty} f_1(R) \sim \cos(kR) \quad , \tag{2.19b}$$

then the Green's function $G_0(R,R')$ is defined by

$$G_0(R,R') = -\frac{2\mu}{\hbar^2 k} f_0(R_<)\, f_1(R_>) \quad . \tag{2.20}$$

Defining the matrix $\underset{\approx}{G}_0$ and vector $\underset{\sim}{f}_0$ by

$$(\underset{\approx}{G}_0)_{i,j} = \langle g_i|G_0|g_j\rangle = \int dR \int dR'\, g_i(R)\, G_0(R,R')\, g_j(R') \tag{2.21a}$$

$$(\underset{\sim}{f}_0)_i = \langle g_i|f_0\rangle = \int dR\, g_i(R)\, f_0(R) \quad , \tag{2.21b}$$

the exact expression for the phast shift δ for the Schrödinger equation (2.17) is

$$\tan\delta = \tan\delta_0 - \frac{2\mu}{\hbar^2 k} \; \underset{\sim}{f}_0 \cdot (\underset{\approx}{1} - \underset{\approx}{A} \cdot \underset{\approx}{G}_0)^{-1} \cdot \underset{\approx}{A} \cdot \underset{\sim}{f}_0 \quad . \tag{2.22}$$

III. Results

Calculations were performed on the Porter-Karplus[7] potential surface for the collinear version of the $H + H_2$ reaction. The asymptotic diatomic potential is a Morse potential in this case, so the vibrational function $\phi(r)$ is the ground state eigenfunction of the Morse oscillator.

The functions $\{u_i\}$ used to expand the non-separable interaction [cf. Eq. (2.16)] were taken to be the set of harmonic oscillator wavefunctions whose parameters were chosen to give the best fit to the kernel. Since the exchange kernel is peaked sharply along the diagonal, as seen in Figure 2, a fairly large expansion is necessary; to achieve three significant figures in the reaction probability, for example, 25 functions were required. It should also be noted that the exchange kernel is energy dependent [cf. Eq. (2.5)], but the separable expansion of it makes it easy to do the calculation for different energies.

The correlation basis set $\{\chi_n\}$ was taken to be a product of harmonic oscillator wavefunctions in the coordinates s and u,

$$s = r_a - r_b$$

$$u = \frac{r_a + r_b}{2} \quad ,$$

which diagonalize the kinetic energy at the saddle point of the potential surface. The index n is thus two indices, $n = (n_s, n_u)$. N_u is the number of functions used in the u coordinate (symmetric stretch), and N_s is the number of functions used in the s coordinate (asymmetric stretch). The total number of correlation functions is thus $N_s \cdot N_u$, although this factors into + and - parity groups corresponding to n_s being even or odd. The parameters of the harmonic oscillator functions were chosen to give the fastest convergence.

Table I shows the phase shifts δ_+ and δ_- obtained with various sizes of the correlation basis. One sees reasonable convergence with quite a small basis set and also observes the effect of the "minimum principle",[5] the fact that δ_+ and δ_- converge monotonically as the basis set is enlarged.

Table II shows the reaction probability as a function of total energy. To show the importance of closed vibrational channels, the "open channels only" result (i.e., no correlation functions) is shown along with the results that have converged with respect to the correlation basis. Also shown are the results obtained earlier by Duff and Truhlar,[8] with which our converged values are in excellent agreement. Numerical error in our calculation is less than 2%, similar to that of Duff and Truhlar. The major source of error in the present calculation arises from the numerical integrations to obtain the matrix elements of the Green's function.

IV. Concluding Remarks

The calculations described in this paper are the first complete application of Miller's formulation of the reactive scattering problem. Only standard Jacobi coordinates are involved, and the rearrangement process is described via a non-local exchange interaction. The effect of energetically closed channels is included through a set of square-integrable correlation functions.

The results show that the method is capable of accurate scattering calculations. Particularly encouraging is the fact that only a small number of correlation functions is necessary to achieve convergence. This is presumably true because the correlation functions, which are chosen specifically to describe the system in the "transition state" region, are more effective in characterizing the wavefunction than closed channels of the asymptotic Hamiltonian.

A not-so-encouraging feature in the present approach is that so many terms are needed in Eq. (2.16) to represent the exchange kernel $V_{ex}(R,R')$ by a separable expansion. A more facile way of dealing with it is probably required before this approach would be practical for calculations in higher dimensions.

Perhaps the greatest utility of this formulation of reactive scattering is its applicability to any bi-molecular reaction without modification of the basic equations. Methods for dealing efficiently with the non-local exchange kernel must be found, however, to make it practically useful. The fact that the exchange kernel is highly localized in coordinate space may suggest simplifying approximations.

References

[*] Supported by the National Science Foundation under Grant CHE76-22621.

[‡] Camille and Henry Dreyfus Teacher-Scholar.

1. J. C. Light and R. B. Walker, J. Chem. Phys. 65, 4272 (1976); J. C. Light, Methods of Computational Physics, edited by B. Alder, S. Fernbach, and M. Rotenberg, (Academic Press, New York, 1971), Vol. 10.
2. G. C. Schatz and A. Kuppermann, J. Chem. Phys. 65, 4624, 4642, 4668 (1976); A. Kuppermann, G. C. Schatz, and M. Baer, J. Chem. Phys. 65, 4596 (1976).
3. M. Baer and D. J. Kouri, Chem. Phys. Lett. 11, 238 (1971); J. Chem. Phys. 56, 1758, 57, 3791 (1972).
4. A. B. Elkowitz and R. E. Wyatt, J. Chem. Phys. 62, 2504, 3683 (1975); S. A. Harms and R. E. Wyatt, J. Chem. Phys. 62, 3162, 3173 (1975).
5. W. H. Miller, J. Chem. Phys. 50, 407 (1969).
6. G. Wolken, Jr., and M. Karplus, J. Chem. Phys. 60, 351 (1974).
7. R. N. Porter and M. Karplus, J. Chem. Phys. 40, 1105 (1964).
8. J. W. Duff and D. G. Truhlar, Chem. Phys. Lett. 23, 327 (1973).

Table I. Phase shifts δ_+/δ_- for (N_u,N_s) Correlation Functions.[a]

Phase Shifts					N_u			
	δ_+	0	1	2	3	4	5	6
	0	1.014						
	2		1.317	1.396	1.406	1.411	1.419	1.419
N_s	4		1.337	1.398	1.421	1.434	1.436	1.436
	6		1.349	1.413	1.430	1.436	1.437	1.438
	8		1.359	1.414	1.431	1.430	1.438	1.437
	10		1.361	1.414	1.431	1.436	1.438	1.438

					N_u			
	δ_-	0	1	2	3	4	5	6
	0	.670						
	1		.670	.670	.670	.670	.670	.670
N_s	3		.687	.677	.683	.685	.686	.687
	5		.703	.680	.684	.686	.687	.687
	7		.674	.681	.685	.686	.687	.688
	9		.674	.682	.685	.686	.687	.688

[a] Total energy E = 0.4898 eV.

Table II. Quantum Mechanical Reaction Probability for Collinear H + H_2 on the Porter-Kaplus Surface.

Total Energy (eV)[a]	Reaction Probability		
	Open Channel Only(b)	Fully Converged(c)	Duff and Truhlar(d)
0.4276	0.00449	0.0174	0.0173
0.4334	0.00655	0.0265	0.0265
0.4465	0.0144	0.0617	--
0.4546	0.0226	0.100	0.101
0.4768	0.0660	0.297	0.297
0.4826	0.0853	0.369	0.371
0.4898	0.1137	0.465	0.465

(a) Zero of energy is the bottom of the asymptotic H_2 potential.

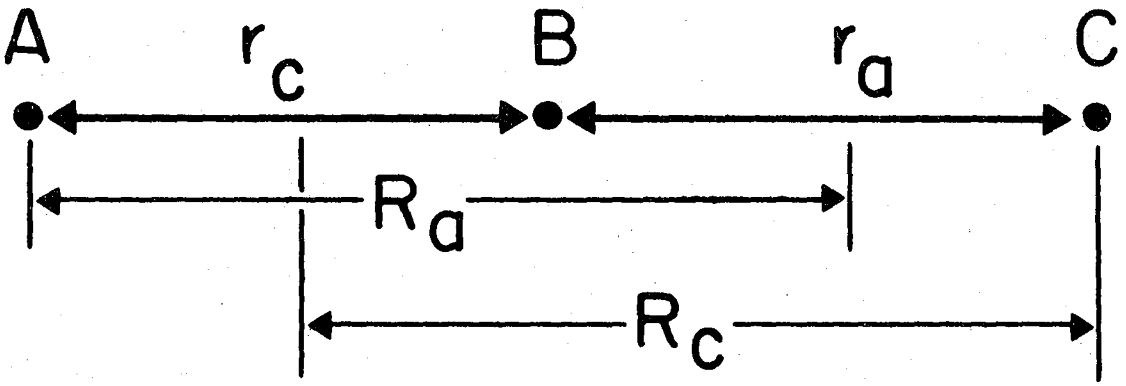
(b) Results obtained with no correlation functions.

(c) Results fully converged with respect to the correlation basis set.

(d) Results of Duff and Truhlar, reference 8.

Figure Captions

1. Depiction of the coordinates (r_a, R_a) and (r_c, R_c) relevant to the collinear A + BC → AB + C reaction.
2. Contour plot of the non-local exchange kernel $V_{ex}(R,R')$ for total energy E = 0.4 eV. R and R' are in units of Bohr radii, a_0.


A
r_c
B
r_a
C
R_a
R_c

XBL 7712-10942

Figure 1

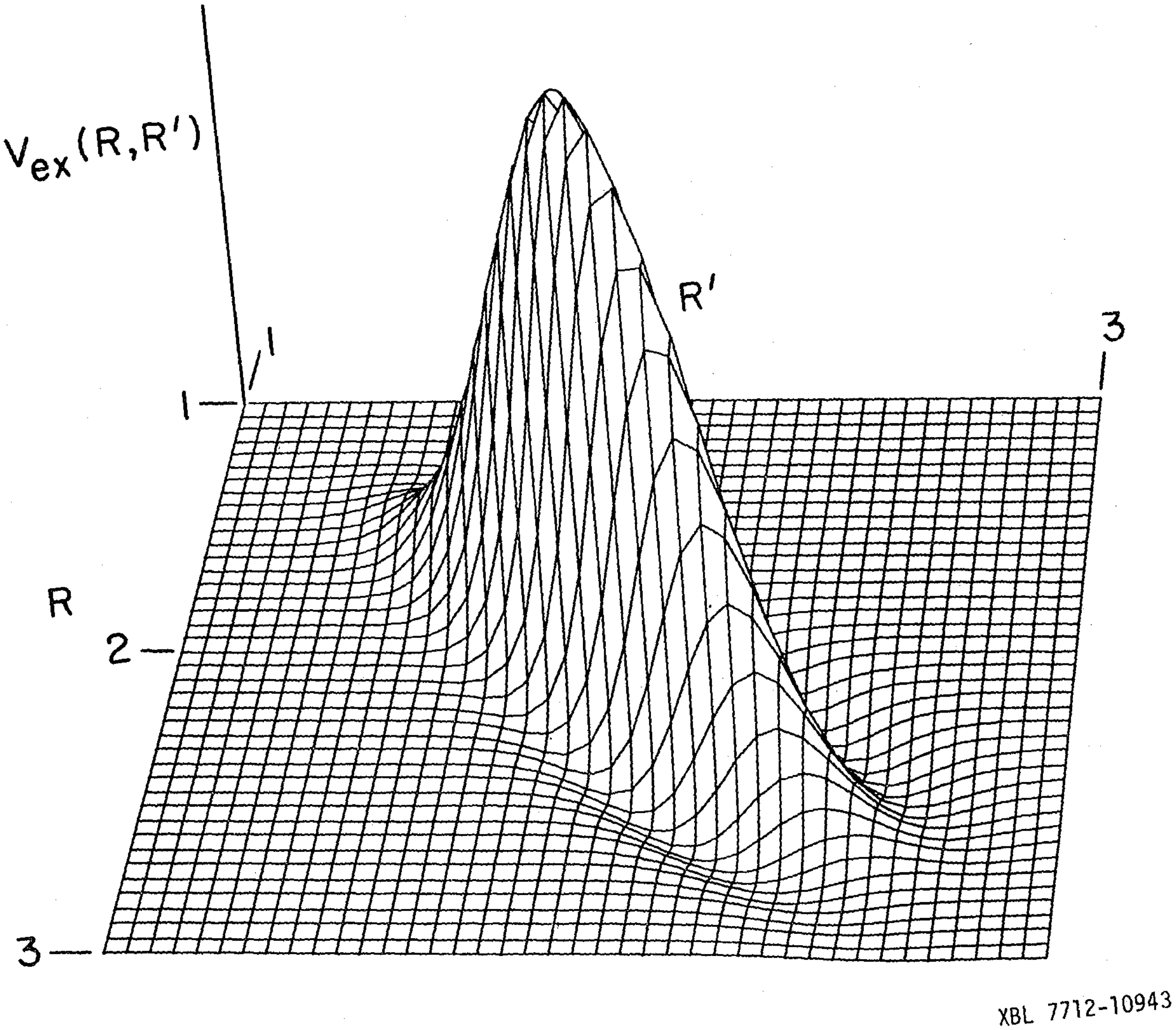


Figure 2

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.