# Variation Procedure for Multichannel Scattering Processes

JOHN H. WEARE* AND EVERETT THIELE†
*Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland*
(Received 2 October 1967)

We present a variation iteration procedure for nonreactive multichannel scattering processes. Its essential features include the expansion of the trial function in terms of the eigenfunctions of a zeroth-order Hamiltonian; the use of the zeroth-order Green's function to impose the correct outgoing behavior on the trial function; and further improvement of the transition matrix element by iteration. The procedure is applied to a problem in atomic-molecular energy exchange.

## INTRODUCTION

VARIATION principles have been of great use in finding approximate solutions in elastic and potential scattering problems.[1] Recently a procedure has been developed for inelastic collisions by Hahn, O'Malley, and Spruch.[2] As yet, however, there seems to be no variation principle emphasizing the use of a linear basis set to expand the scattering solution. In view of the extreme simplicity of variations within a linear basis set, it seems appropriate to advance such a procedure. The method outlined here emphasizes the use of the Hulthén-Kohn procedure, in which one extremizes a functional depending on both an incoming and an outgoing trial function. By using an appropriate Green's function and a projection operator, we are able to insure that the outgoing trial functions satisfy the correct outgoing boundary conditions, while remaining almost entirely in the subspace spanned by our linear basis set. The solution resulting from our variational procedure is then used to calculate the transition matrix elements in several different ways. One of these bears considerable resemblance to the Sokolov method of solving integral equations.[3]

## METHOD

We assume that the scattering system is described by a Hamiltonian ($H=H_1+W_1$) which can be partitioned into an unperturbed part $H_1$, and a short-range potential $W_1$. The quantities of direct physical interest are the transition matrix elements[4]

$$T_{\mathbf{k},l\to\mathbf{k}',n}-T^1{}_{\mathbf{k},l\to\mathbf{k}',n}=\langle\chi^-{}_{\mathbf{k}',n}|W_1|\psi^+{}_{\mathbf{k},l}\rangle$$
$$=\langle\psi^-{}_{\mathbf{k}',n}|W_1|\chi^+{}_{\mathbf{k},l}\rangle. \quad (1)$$

Here the $\chi$'s are eigenfunctions of $H_1$ and the $\psi$'s are eigenfunctions of $H$. Functions with a superscript $+(-)$ satisfy the appropriate outgoing (incoming) boundary conditions; these functions describe a collision in which the momentum of the scattered particle is $\hbar\mathbf{k}(\hbar\mathbf{k}')$ and the internal state of the target is $l(n)$ before (after) the collision event. $T^1{}_{\mathbf{k},l\to\mathbf{k}',n}$ is the contribution to $T$ as determined by the asymptotic behavior of $\chi$.

In the Hulthén-Kohn variation procedure[1] for computing the transition matrix element, the functional

$$\Gamma_{\mathbf{k},l\to\mathbf{k}',n}=-{}^{\mathrm{tr}}\langle\phi^-{}_{\mathbf{k}',n}|E-H|\psi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}+T_{\mathbf{k},l\to\mathbf{k}',n}{}^{\mathrm{tr}} \quad (2)$$

is made stationary. An arbitrary variation in the trial function ${}^{\mathrm{tr}}\langle\phi^-{}_{\mathbf{k}',n}|$ is allowed. The variation in the trial function $|\psi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}$ is restricted to functions which satisfy the same type of boundary conditions as the exact $|\psi^+{}_{\mathbf{k},l}\rangle$. It must be incoming in channel $l$ and outgoing in the open channels $n$. $T_{\mathbf{k},l\to\mathbf{k}',n}{}^{\mathrm{tr}}$ is the trial value of the transition matrix element as determined by the asymptotic behavior of $|\psi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}$. If either ${}^{\mathrm{tr}}\langle\phi^-{}_{\mathbf{k}',n}|$ or $|\psi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}$ is exact, then $\Gamma_{\mathbf{k},l\to\mathbf{k}',n}=T_{\mathbf{k},l\to\mathbf{k}',n}$. For approximate functions the value of $\Gamma$ is taken as an approximation to the $T$ matrix element.

We now consider a method of picking trial $\psi$'s which automatically satisfy the correct boundary conditions. We let

$$|\psi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}=|\chi^+{}_{\mathbf{k},l}\rangle+PG_1{}^+W_1|\phi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}, \quad (3)$$

with arbitrary $\phi$. Here

$$G_1{}^+=\lim_{\epsilon\to 0}\frac{1}{E-H_1+i\epsilon}$$

and $P$ is some projection operator. We postpone a complete description of $P$ and here note only that $P$ is assumed to commute with $H_1$. For the trial function given in Eq. (3) one easily shows

$$T_{\mathbf{k},l\to\mathbf{k}',n}{}^{\mathrm{tr}}=T^1{}_{\mathbf{k},l\to\mathbf{k}',n}+\langle\chi^-{}_{\mathbf{k}',n}|PW_1|\phi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}. \quad (4)$$

Substitution of Eqs. (3) and (4) into Eq. (2) yields

$$\Gamma_{\mathbf{k},l\to\mathbf{k}',n}=T^1{}_{\mathbf{k},l\to\mathbf{k}',n}$$
$$+\langle\chi^-{}_{\mathbf{k}',n}|PW_1|\phi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}+{}^{\mathrm{tr}}\langle\phi^-{}_{\mathbf{k}',n}|W_1|\chi^+{}_{\mathbf{k},l}\rangle$$
$$-{}^{\mathrm{tr}}\langle\phi^-{}_{\mathbf{k}',n}|PW_1-W_1PG_1{}^+W_1|\phi^+{}_{\mathbf{k},l}\rangle^{\mathrm{tr}}. \quad (5)$$

In this form the variation principle, like the Lippmann-Schwinger principle[4] which it closely resembles, is stationary with respect to arbitrary variations in the $\phi$'s.

Consider now trial $\phi$'s of the form

$${}^{\mathrm{tr}}\langle\phi_{\mathbf{k}',n}{}^-|=\sum_s N_s\langle\chi_j{}^-|$$

* Sonneborn Fellow.
† Alfred P. Sloan Fellow.
[1] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964).
[2] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **134**, B911 (1964).
[3] A. Yu. Luchka, *The Method of Averaging Functional Corrections: Theory and Applications* (Academic Press Inc., New York, 1965).
[4] The notation and terminology used in this work is that of A. Messiah, *Quantum Mechanics* (North-Holland Publishing Co., Amsterdam, 1962), Vol. 2.

TABLE I. Collisionally induced vibrational transition probabilities.

| Transition[a] | $E$[b] | $\alpha$[c] | $m$[d] | No. of oscillator levels[e] | Eq. (4) $P$ | Eq. (9) $P$ | Iterated $P$ | $P_{Ex}$[f] | Second-order Born[g] | No. of basis functions |
|---|---|---|---|---|---|---|---|---|---|---|
| $1\rightarrow 2$ | 6.00 | 0.114 | 0.5 | 5 | $0.451\times10^{-4}$ | $0.130\times10^{-2}$ | $0.130\times10^{-2}$ | $0.132\times10^{-2}$ | $0.200\times10^{-2}$ | 90 |
| $0\rightarrow 1$ | 6.00 | 0.114 | 0.5 | 4 | $0.2325\times10^{-2}$ | $0.289\times10^{-2}$ | $0.289\times10^{-2}$ | $0.285\times10^{-2}$ | $0.341\times10^{-2}$ | 75 |
| $0\rightarrow 1$ | 6.00 | 0.114 | 0.5 | 2 | $0.224\times10^{-4}$ | $0.8112\times10^{-3}$ | $0.246\times10^{-2}$ | $0.285\times10^{-2}$ | $0.341\times10^{-2}$ | 41 |
| $0\rightarrow 2$ | 8.00 | 0.300 | 2/3 | 6 | 0.37014 | 0.2109 | 0.21104 | 0.291 | 7.03 | 90 |

[a] $i\rightarrow j$ indicates initial oscillator state $i$ and final oscillator state $j$.
[b] Total energy of system in units of $\hbar\omega$.
[c] Parameter indicating strength of interaction. See Ref. 7.
[d] Mass ratio parameter. See Ref. 7.
[e] Number of harmonic-oscillator levels included in the projection operator and the basis set $|j\rangle$.
[f] See Ref. 7.
[g] See Ref. 6.

and

$$|\phi_{\mathbf{k},i}{}^{+}\rangle^{\mathrm{tr}}=\sum_j L_j|\chi_j{}^{+}\rangle.$$

Here we label some finite set of functions chosen from the continuum of $\chi$'s with a discrete parameter which denotes both internal state and momentum. Since the $\phi$'s need only be correct in that region of space where $W_1$ is non-negligible, one can rationalize the use of a discrete set of momentum values in the trial function. In practice, of course, one is always limited to a finite number of basis functions.

Using the above $\phi$'s in Eq. (5) and making $\Gamma_{\mathbf{k},l\rightarrow\mathbf{k}',n}$ stationary with respect to variations in the $L_j$ and $N_j$, we find

$$\langle\chi_s{}^{-}|PW_1|\chi_{\mathbf{k},i}{}^{+}\rangle-\sum_j L_j \times\langle\chi_s{}^{-}|PW_1-W_1PG_1{}^{+}W_1|\chi_j{}^{+}\rangle=0, \quad (6)$$

$$\langle\chi_{\mathbf{k}',n}{}^{-}|W_1|\chi_j{}^{+}\rangle-\sum_j N_j \times\langle\chi_s{}^{-}|PW_1-W_1PG_1{}^{+}W_1|\chi_j{}^{+}\rangle=0. \quad (7)$$

Equations (6) and (7) may be solved numerically for the $L_j$ and $N_j$. Because of Eq. (7), and ultimately because of the linear form of the trial functions, one finds

$$\Gamma_{\mathbf{k},l\rightarrow\mathbf{k}',n}=T^{\mathrm{tr}}{}_{\mathbf{k},l\rightarrow\mathbf{k}',n}. \quad (8)$$

We see then that the approximate value for the $T$ matrix element is determined completely by the long-range behavior of our trial function [Eq. (3)].

One can also determine an approximate value for the $T$ matrix element by substituting our trial function into Eq. (1). This method, which looks at the short-range behavior of the trial function, gives

$$T_{\mathbf{k},l\rightarrow\mathbf{k}',n}-T^{1}{}_{\mathbf{k},l\rightarrow\mathbf{k}',n}\cong\langle\chi^{-}{}_{\mathbf{k}',n}|W_1|\chi^{+}{}_{\mathbf{k},l}\rangle +\langle\chi^{-}{}_{\mathbf{k}',n}|W_1PG_1{}^{+}W_1|\phi^{+}{}_{\mathbf{k},l}\rangle. \quad (9)$$

Still a third approximation to the $T$ matrix element can be arrived at by the following considerations. If we put $\phi=P\psi$ in Eq. (3), then that equation becomes identical to the integral scattering equation[4] for a system with Hamiltonian $PHP$. We can therefore regard $\phi$ itself as an approximation to $\psi$. Iterating $\phi$ once in the integral scattering equation for Hamiltonian $H$ and using Eq. (1) gives an approximate $T$ which is identical with the result given in Eq. (9), except that the $P$ operator does not appear in the second term on the right-hand side. This approximation, which we shall refer to as $T$ (iterated), arises in a very natural way in the Sokolov method.[3]

## APPLICATION

We have carried out some preliminary calculations for the inelastic scattering of an atom $A$ and a diatomic molecule $BC$ in a collinear collision. The Hamiltonian for this system, with coordinates as shown in Fig. 1, is

$$H=(1/2\mu_y)P_y{}^2+(1/2\mu_x)P_x{}^2+U(y)+V(x,y),$$

where $\mu_x$ and $\mu_y$ are reduced masses. $U(y)$ is the vibrational potential function for the diatomic $BC$. $V(x,y)$ is the short-ranged interaction potential between $A$ and $BC$. We assume as in Refs. 5–7 that $V(x,y)$ acts only between atoms $A$ and $B$ and is of the form $V(x,y)=Ce^{-ax}$ and that $U(y)=\frac{1}{2}ky^2$. For the unperturbed Hamiltonian we take

$$H^1=P_x{}^2/2\mu_x+P_y{}^2/2\mu_y+U(y)+V(x,y_{\mathrm{eq}}),$$

where $y_{\mathrm{eq}}$ is the equilibrium extension of the harmonic oscillator. The eigenvalue problem $H^1|\chi_{k,l}\rangle=E|\chi_{k,l}\rangle$ has been solved by Jackson and Mott.[5] The solutions are products of harmonic-oscillator functions $|l\rangle$, and stationary distorted waves $|k\rangle$. In selecting the basis set $|j\rangle$ one must decide how many harmonic-oscillator functions are to be included in the products. We choose the operator $P$ to project onto these same harmonic-oscillator states, $P=\sum|l\rangle\langle l|$. In the general problem, we envisage the operator $P$ to be a projection operator onto the space spanned by those internal states which

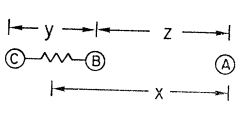


FIG. 1. Coordinate system for the collinear collision of an atom and a diatomic molecule. $x$ is the distance from $A$ to the center of mass of $BC$.

[5] J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703 (1932).
[6] E. Thiele and J. H. Weare, J. Chem. Phys. (to be published).
[7] D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).

are included in the basis set. The matrix elements $\langle\chi_{k'n}|W_1|\chi_{k,l}\rangle$ have been computed in Ref. 5. $\langle\chi_{k',n}|\times W_1PG_1{}^+W_1|\chi_{k,l}\rangle$ is evaluated numerically as described in Ref. 6. Equations (6) and (7) may then be solved and the three variation probabilities computed. In Table I we compare the results of a few such calculations with Secrest and Johnson exact values.[7] We note a remarkable improvement in Eq. (9) over Eq. (4). The value given by Eq. (4) may be improved somewhat by using a trial $\phi$, $|\phi^+{}_{kl}\rangle=|\chi_{kl}\rangle+\sum L_j|\chi_j\rangle$, where $j$ does not include $|\chi_{k,l}\rangle$. In all calculations where we included just a very few oscillator levels in the trial function (as in entry 3 of Table I), it was the inclusion of the projection operator in Eq. (3) which proved to be the essential step in obtaining a reasonably accurate value for the iterated $P$. In the calculations reported in Table I we have included enough momentum values for each oscillator state to ensure convergence to about 5% accuracy in the iterated $P$ and the $P$ calculated from Eq. (9).

PHYSICAL REVIEW VOLUME 167, NUMBER 1 5 MARCH 1968

# Calculation of Energy Levels Which Arise from the $p^2$ Configuration of the Ground State of Carbon. Multiconfiguration Hartree-Fock Calculations

P. S. BAGUS* AND C. M. MOSER
*Centre de Mecanique Ondulatoire Appliquee, Paris, France*
(Received 13 September 1967)

A calculation of the term splitting $(^3P\text{-}^1D)/(^1D\text{-}^1S)$ for the $p^2$ ground-state configuration of carbon using Hartree-Fock radial orbitals gives an error of 21% when compared with experiment. Multiconfiguration Hartree-Fock calculations where the excitations are confined to the $2p^2$ shell reduces the error to slightly more than 1%.

## I. INTRODUCTION

WHEN Hartree-Fock (HF) wave functions are used to calculate the relative energy levels of the different terms which arise from a given configuration, the results are generally in poor agreement with experiment; e.g., in the $p^2$ ground-state configuration in carbon the $^3P-{}^1D$ transition is in error by somewhat less than 30%, the $^3P-{}^1S$ transition by somewhat more than 40%.

Evidently a correlated function must be used to study this problem. Two approaches to the introduction of correlation into the wave function may be used. One could try to calculate very good approximate wave functions which include nearly all the correlation energy, or one could try to calculate wave functions for the three states mentioned above which would have very nearly the *same errors* in their energies. Although the absolute errors in the total energies may be relatively large, the errors in the *differences* in the total energies for all three states would be small. The second approach seems to us to be preferable since it is certainly much more likely to be extendable to large systems.

Even though methods are now available to obtain a very large fraction (>90%) of the correlation energies of the closed-shell configuration $^1S$ states of first-row atoms, the extension to states which arise from open-shell configurations even of first-row atoms presents formidable difficulties in practice if not in principle. The term splitting in the ground-state configurations of first-row atoms is not a very exciting physical problem. Interesting problems only arise much farther down the periodic table where it would be extremely difficult to try to use many if not most of the methods which have been used for calculating wave functions for the $^1S$ ground states of He and Be.

The difficulty in applying an approximate method (like HF) to physical problems is not so much that errors are introduced but that the errors are different for different states. For many problems all one really needs to do is to modify the approximate method so as to obtain a roughly constant error. Thus, in the study of energy levels which arise from the same configuration we need only add enough correlation energy so that we find roughly the same error in each state.

The method which seems to us most promising to fulfill this goal at the present time is the multiconfiguration Hartree-Fock method (MCHF). In this method variational equations are solved for both the orbitals which are used to construct the configurations and the coefficients of the configurations in the wave functions. Iterations are repeated until self-consistent values are obtained for both orbitals and configuration-mixing coefficients. The procedure was probably first described by Frenkel[1] and the first calculations were carried out with two configurations for some states of 0, $0^+$, and $0^{++}$ by Hartree, Hartree, and Swirles.[2] Since the 1940's MCHF calculations on atomic energy levels have been

* Maître de Conférence Associé in the Sorbonne, 1966–67.

[1] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, England, 1934).

[2] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **A238**, 223 (1939).