structure is in striking agreement with that of Hall and Reinhardt[10] for the case of N_2 which is isoelectronic to CO.

The "bump" observed at the lowest energy occurs at the location of the ground state of the "transient" negative ion or higher. This would allow the assignment of an upper limit to the electron affinity of CO. In Fig. 1 there is a definite bump at 1.8 eV and possibly another at ~1.6 eV. This experiment assigns the value of -1.8 ± 0.1 eV as an upper limit for the electron affinity of CO. The possibility of another "bump" at 1.6 eV may reduce this value when greater sensitivity is achieved.

The author wishes to thank Professor Joseph Kaplan for continued support during the course of this research, and is deeply indebted to Professor Donald Villarejo for interesting and stimulating discussions concerning the interpretation of the data.

---

*Work supported in part by the Geophysics Research Directorate, Air Force Cambridge Research Laboratories, Office of Aerospace Research, U. S. Air Force.

[1]G. J. Schulz, Phys. Rev. 116, 5, 1141 (1959).

[2]J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).

[3]J. T. Dowell and T. E. Sharp, J. Chem. Phys. 47, 12, 5068 (1967).

[4]G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, N.J., 1950).

[5]H. H. Brongersma and L. J. Oosterhoff, Chem. Phys. Letters 1, 169 (1967).

[6]The mechanism by which the trapped electrons reach the collector plate is a diffusion mechanism due to collisions. An electron which lacks sufficient energy to escape in the axial direction collides with gas molecules until it finally reaches the collector plate or "center" plate of the parallel-plate assembly. It was observed that a small electric field of the order of ~1 V/cm made the trapped electrons vanish. This was attributed to the $\vec{E} \times \vec{B}$ drift velocity given to all charged particles within the region where the electric field exists. The value of the electric field at which the trapped-electron current vanishes together with the magnitude of the magnetic field and information concerning the width of the plates and their distance from the electron beam leads to an estimation of the rate of diffusion due to collisions across the magnetic field.

[7]The work of D. Rapp and D. D. Briglia [J. Chem. Phys. 43, 1480 (1965)] and the more recent work of P. J. Chantry [Phys. Rev. 172, 125 (1968)] both establish the position of the peak in dissociative attachment in CO at 9.9 eV.

[8]Rapp and Briglia, Ref. 7.

[9]G. J. Schulz, Phys. Rev. 135, A988 (1964).

[10]J. Hall and J. Reinhardt, Compt. Rend. B266, 744 (1968).

EXPANSION TECHNIQUE FOR INELASTIC SCATTERING*

Frank E. Harris
Department of Physics, University of Utah, Salt Lake City, Utah 84112

and

H. H. Michels
United Aircraft Research Laboratories, East Hartford, Connecticut 06108

(Received 3 January 1969)

A nonarbitrary method is presented for the calculation of inelastic-scattering wave functions by an expansion technique. The method can be applied for any incident energy, including values at resonances resulting from stable or metastable bound states. Calculations are presented for an exactly soluble two-channel model problem which illustrates the utility of the method.

A central objective in the development of expansion methods for treating nonrelativistic quantum-mechanical scattering is the identification of optimum criteria for defining the expansion coefficients. The well-known variational methods of Kohn[1] and Hulthén[2] are arbitrary in the sense that they are two of an infinite set of prescriptions leading to phase shifts whose errors are of second order. Moreover, the variational criterion alone is not sufficient to guarantee in any reasonable sense an optimum wave function, as is evidenced by the convergence problems[3] exhibited by the Kohn method. The difficulties are, at least in part, due to the approximation of a continuous-spectrum Hamiltonian by a finite-dimensional projection thereof whose discrete spectrum does not necessarily contain an a priori–selected scattering energy. This consideration led one of the present authors to propose a method for selecting scattering en-

ergies at which expansion calculations would proceed favorably,[4] and this method has led to rapidly convergent descriptions of elastic-scattering processes.[5] However, the method is limited to elastic scattering, and it is not always easy to obtain results for predetermined scattering energies. Nesbet[6] has recently contributed a valuable discussion of the various expansion methods, explicitly pointing out the conditions which lead to divergence in the Kohn method and indicating how to avoid the divergence problem. Nesbet's approach also has the great advantage that it can be applied to multichannel processes[7] as well as to elastic scattering, but, like other variational methods, it contains a measure of arbitrariness.

The present communication reports a method designed to yield unique optimum-expansion approximations for both elastic and inelastic scattering processes at arbitrary energy. For a central-field Hamiltonian H of finite range (as would be encountered, for example, in electron-atom scattering) and a given energy E, we consider approximate stationary-state wave functions ψ, of definite angular momentum, of the general form

$$\psi = \sum_{i=1}^{2n} a_i \varphi_i + \sum_{i=1}^{m} b_i \eta_i. \tag{1}$$

Here the φ_i are the complete set of asymptotic eigenfunctions (unbound states) appropriate to energy E, and the η_i are quadratically integrable (short-range) functions needed to approximate ψ within the range of H. There will be two asymptotically orthogonal φ_i for each of n ($n \geq 1$) open scattering channels, and m, the number of η_i, will be dictated by the accuracy desired. We assume the η_i to be orthonormal, and the φ_i to be both orthogonalized to all η_i and scaled to equal asymptotic intensity.

In an n-channel problem there will be n different stationary-state wave functions to be approximated as in Eq. (1). All scattering processes can be characterized from the a_i coefficients of these wave functions since the a_i define the relative amplitudes and phases in the various channels. To determine the wave functions, we assume $(H-E)\psi$ to be described by the expansion

$$(H-E)\psi = \sum_{i=1}^{2n} c_i \varphi_i + \sum_{i=1}^{m} d_i \eta_i. \tag{2}$$

Equation (2) amounts to the assumption that short-range functions beyond those important in ψ do not contribute appreciably to $(H-E)\psi$. However, even though $(H-E)\psi$ is inherently a short-range function, it is crucial to retain the φ_i in Eq. (2), as expansions containing only a finite number of η_i cannot describe general behavior in the transition region at the edge of the range of H.

We require relations connecting the a_i and b_i to the c_i and d_i. Substituting Eq. (1) into Eq. (2) and taking scalar products with the η_i, we reach

$$\mathsf{M}_{\eta\varphi} a + \mathsf{M}_{\eta\eta} b = d, \tag{3}$$

where $\mathsf{M}_{\eta\varphi}$ and $\mathsf{M}_{\eta\eta}$ are matrices of elements $\langle \eta_i | H-E | \varphi_j \rangle$ and $\langle \eta_i | H-E | \eta_j \rangle$, respectively, and a, b, and d are vectors of coefficients a_i, b_i, and d_i. Expressions for the c_i are obtained in a less straightforward manner, as the φ_i are not quadratically integrable, and moreover our aim is to use the c_i to optimize the representation of ψ within the range of H. We therefore restrict the range of Eq. (2) to a finite volume larger than the range of H and determine the c_i by taking scalar products with the φ_i. If the range of Eq. (2) is sufficiently large, the asymptotic orthogonality and equal intensity of the φ_i will cause $\langle \varphi_i | \varphi_j \rangle$ to approach $N\delta_{ij}$, where N depends on the range of Eq. (2) but is independent of i and j. The equation for the c_i then takes the form

$$\mathsf{M}_{\varphi\varphi} a + \mathsf{M}_{\varphi\eta} b = Nc, \tag{4}$$

where $\mathsf{M}_{\varphi\varphi}$, $\mathsf{M}_{\varphi\eta}$, and c are defined analogously to the quantities in Eq. (3). We note that as the range of Eq. (2) is increased, the left side of Eq. (4), which contains only convergent integrals, will approach a finite value, while the factor N on the right side increases without limit. We therefore conclude that c will vary as N^{-1} as will $N|c|^2$ (vide infra).

We now seek the set of coefficients a and b which minimizes the norm of $(H-E)\psi$ for a fixed scale of ψ. It is not possible simply to set $(H-E)\psi$ to zero because E is not necessarily in the spectrum of the projection of H defined by the expansion functions. For general c and d, the norm of $(H-E)\psi$ over a given range of Eq. (2) is $(N|c|^2 + |d|^2)^{1/2}$, and because $N|c|^2$ varies as N^{-1}, the $|d|^2$ term dominates as this range is increased. Thus our optimum specification of the minimum-norm condition is to set $d = 0$ and make c minimum. We now show that the condition $d = 0$ is an acceptable solution that can be imposed for arbitrary E.

Application of the minimum-norm condition depends upon whether the matrix $\mathsf{M}_{\eta\eta}$ is singular.

When $M_{\eta\eta}$ is nonsingular, the condition $d=0$ can be inserted into Eq. (3), which then has solution $b = -M_{\eta\eta}^{-1}M_{\eta\varphi}a$. Substituting this result into Eq. (4), we have

$$(M_{\varphi\varphi}-M_{\varphi\eta}M_{\eta\eta}^{-1}M_{\eta\varphi})a = Nc. \tag{5}$$

Multiplying each member of Eq. (5) by its adjoint,

$$a^{\dagger}(M_{\varphi\varphi}-M_{\varphi\eta}M_{\eta\eta}^{-1}M_{\eta\varphi})^{\dagger}(M_{\varphi\varphi}-M_{\varphi\eta}M_{\eta\eta}^{-1}M_{\eta\varphi})a = N^2|c|^2 \tag{6}$$

so that a is to be chosen to minimize the left member of Eq. (6). For an n-channel process, we will need n such a vectors. They are optimally given as the n eigenvectors of smallest eigenvalue of the Hermitian matrix

$$(M_{\varphi\varphi}-M_{\varphi\eta}M_{\eta\eta}^{-1}M_{\eta\varphi})^{\dagger}(M_{\varphi\varphi}-M_{\varphi\eta}M_{\eta\eta}^{-1}M_{\eta\varphi}).$$

When $M_{\eta\eta}$ is singular, the foregoing discussion must be modified. Singular $M_{\eta\eta}$ will arise for certain E values, which may be of interest in connection with resonances or because the calculations may be carried out more accurately at these energies. We illustrate by considering the case where one vector, b_0, is annihilated by $M_{\eta\eta}$. Then Eq. (3) with $d=0$ has solution

$$b = kb_0-(M_{\eta\eta}+\alpha b_0 b_0^{\dagger})^{-1}M_{\eta\varphi}a, \tag{7}$$

with α and k arbitrary (except that $\alpha\neq 0$). The value of α does not actually influence b; its presence merely enables the inverse to have meaning. Equation (3) also leads to

$$b_0^{\dagger}M_{\eta\varphi}a = 0, \tag{8}$$

which helps indicate why b does not really depend upon α. For the case under consideration, Eqs. (7) and (8) together define the same conditions as Eq. (3) with $d=0$. Inserting Eq. (7) into Eq. (4) we obtain

$$Ma+ke = Nc, \tag{9}$$

where $M = M_{\varphi\varphi}-M_{\varphi\eta}(M_{\eta\eta}+\alpha b_0 b_0^{\dagger})^{-1}M_{\eta\varphi}$ and $e = M_{\varphi\eta}b_0$. We now vary a to minimize $|c|$ as given by Eq. (9), subject to Eq. (8) and a scale condition which we may take to be $a^{\dagger}a=1$. For a single-channel process, a is of dimension 2 and is therefore completely determined by Eq. (8) and the scale condition. This situation corresponds to our previous approach,[4] in which E was set to make $M_{\eta\eta}$ singular.

For n-channel processes ($n>1$), a nontrivial minimization of $|c|$ must be carried out. If it so happens that $e=0$, then Eq. (8) is automatically satisfied and a discussion similar to that at Eqs. (5) and (6) identifies optimum a vectors as the n minimum-eigenvalue eigenvectors of $M^{\dagger}M$. If $e\neq 0$, a minimization by the method of Lagrange multipliers leads to

$$a = \mu\left(M^{\dagger}M-\frac{M^{\dagger}ee^{\dagger}M}{e^{\dagger}e}-\lambda I\right)^{-1}e \tag{10}$$

with μ chosen to make $a^{\dagger}a=1$ and λ chosen so that

$$e^{\dagger}\left(M^{\dagger}M-\frac{M^{\dagger}ee^{\dagger}M}{e^{\dagger}e}-\lambda I\right)^{-1}e = 0. \tag{11}$$

The λ values satisfying Eq. (11) can be proven non-negative, and $|c|^2$ can be shown to be proportional to λ. The n a vectors of smallest $|c|$ thus correspond to the smallest λ values. These λ values may actually be determined by finding the eigenvalues λ_i and eigenvectors f_i of $M^{\dagger}M-M^{\dagger}ee^{\dagger}M/e^{\dagger}e$, in terms of which Eq. (11) becomes the easily soluble algebraic equation $\sum_i |e^{\dagger}f_i|^2/(\lambda_i-\lambda)=0$.

The foregoing analysis indicates how, for an n-channel problem, the minimum-norm condition leads uniquely, for any energy, to n approximate scattering wave functions specified asymptotically by the coefficients a. Linear combinations of these n wave functions can be taken so as to form "channel" functions ψ_i. The vector a_i for channel i is characterized, for the asymptotic functions regular at the origin, by unit amplitude in channel i and zero amplitude in all other channels. From such a set of a_i a reactance matrix R and elastic and inelastic cross sections can be obtained by standard methods.[8]

It is now possible, following ideas introduced by Kato,[9] to make a first-order correction to the R matrix which leaves it in symmetric form and

Table I. Elements of the R matrix and cross sections for elastic and inelastic scattering. m denotes the number of expansion functions.

	R_{11}	$R_{12}=R_{21}$	R_{22}	$Q_{11}(\pi a_0^2)$	Q_{12}	Q_{21}	Q_{22}
M = 1	3.03672	- 2.26139	1.18916	1.90365	0.84801	3.39205	2.43583
2	-36.65395	23.71994	-15.79199	2.15455	0.75478	3.01911	2.74710
3	10.47830	- 6.92822	4.13531	2.14241	0.78145	3.12581	2.53334
4	16.06741	-10.46549	6.37432	2.16859	0.76946	3.07785	2.56148
5	17.95694	-11.68783	7.16861	2.16598	0.76946	3.07786	2.55658
6	18.47464	-12.03122	7.39666	2.16409	0.76982	3.07926	2.55950
7	18.69504	-12.16398	7.47660	2.16561	0.76928	3.07712	2.55644
8	19.22830	-12.49501	7.68199	2.16795	0.76835	3.07340	2.55526
9	19.92332	-12.94302	7.97126	2.16778	0.76814	3.07256	2.55619
10	20.36053	-13.23003	8.15975	2.16691	0.76824	3.07294	2.55858
Exact	21.76525	-14.12742	8.73385	2.16791	0.76746	3.06985	2.55844

results in significantly improved cross sections. Letting R stand for the corrected, and R^0 for the uncorrected reactance matrices, the corrections satisfy

$$R_{ij} = R_{ij}^{0} - 2(k_i k_j)^{-1/2} a_i^{\dagger} M a_j, \tag{12}$$

where $a_i^{\dagger} M a_j$ is equivalent to $\langle \psi_i | H-E | \psi_j \rangle$. Here M is defined as in Eq. (9), with $\alpha \neq 0$ if $M_{\eta\eta}$ is singular and $\alpha = 0$ otherwise. The quantities k_i and k_j are the magnitudes of the wave vectors for channels i and j.

To demonstrate the utility of the analysis presented here, we give results obtained for an exactly soluble two-channel-model problem used by Huck[10] and more recently by Nesbet[7] to test the convergence of several variational approaches to inelastic scattering. This problem is defined in one dimension over the range $0 \leq r \leq \infty$, with Hamiltonian

$$H = \sum_{i,j=1}^{2} |\chi_i\rangle H_{ij} \langle \chi_j|, \quad \langle \chi_i | \chi_j \rangle = \delta_{ij},$$

and $H_{11} = -\frac{1}{2}(d^2/dr^2)$, $H_{22} = -\frac{1}{2}(d^2/dr^2) + 0.375$, $H_{12} = H_{21} = \frac{1}{2}C$ $(r < 1)$, and $H_{12} = H_{21} = 0$ $(r > 1)$. Before imposing orthogonality and normalization conditions, the asymptotic functions chosen were $\varphi_1 = |\chi_1\rangle \sin k_1 r$, $\varphi_2 = |\chi_1\rangle(1-e^{-r})\cos k_1 r$, $\varphi_3 = |\chi_2\rangle \times \sin k_2 r$, and $\varphi_4 = |\chi_2\rangle(1-e^{-r})\cos k_2 r$. The short-range functions were taken as

$$\eta_i = |\chi_1\rangle r^i \exp(-\alpha_i r);$$

$$\eta_{m+i} = |\chi_2\rangle r^i \exp(-\alpha_i r), \quad i = 1, \cdots, m, \tag{13}$$

with expansion lengths up to a maximum of m. A constant value of $\alpha_i = 2.5$ proved to give the best rate of convergence.

The calculated cross sections are illustrated in Table I for the case studied by Huck with $C^2 = 10.0$, $k_1 = 1.0$, and $k_2 = 0.5$. It is found that more rapid convergence is obtained for the cross sections than for the individual elements of the R matrix. Uniform convergence of the R matrix is observed with increasing expansion lengths. Further studies of inelastic-scattering processes in an atomic problem are now being carried out using this proposed minimum-norm procedure.

We wish to acknowledge helpful discussions with Dr. H. J. Kolker and with Dr. R. K. Nesbet, who suggested the use of the model problem chosen here.

*Work supported in part by the U. S. Air Force Office of Scientific Research of the Office of Aerospace Research under Contract No. AF49(638)-1711.

[1]W. Kohn, Phys. Rev. 74, 1763 (1948).

[2]L. Hulthén, Kgl. Fysiograf. Sällskap. Lund, Förh. 14, No. 8 (1944).

[3]C. Schwartz, Ann. Phys. (N.Y.) 16, 36 (1961).

[4]F. E. Harris, Phys. Rev. Letters 19, 173 (1967).

[5]H. H. Michels and F. E. Harris, Phys. Rev. Letters 19, 885 (1967).

[6]R. K. Nesbet, Phys. Rev. 175, 134 (1968).

[7]R. K. Nesbet, private communication.

[8]N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, New York, 1965).

[9]T. Kato, Progr. Theoret. Phys. (Kyoto) 6, 394 (1951).

[10]R. J. Huck, Proc. Phys. Soc. (London), Ser. A 70, 369 (1957).