

The strong-coupling method in the theory of electron-atom collisions

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A review is presented of the present status of calculations, performed by the strong-coupling method, of the cross sections of electron-atom collisions. The main principles of the method are described, together with the procedures used for numerical calculations and with the properties of the results. The atoms for which calculations have been performed to date, and under what approximations, are reported and the published references are cited. The main problems arising in the calculations are discussed together with the methods used to resolve them. Proposed generalizations of the strong-coupling method are considered.

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1. INTRODUCTION

In quantum mechanics, the scattering of an electron by an atom is described by an equation of rather simple form: a Schrödinger equation containing the Coulomb interaction potential of all the electrons among themselves and with the nucleus. Yet it is a differential equation in the partial derivatives of many variables, and considerable mathematical difficulties arise in actually solving it. As long as the energy of the incident electron greatly exceeds the energy of the atomic electrons, there is no problem: the incident electron flies past the atom so quickly that it does not succeed in changing appreciably the states of the atomic electrons, and a fortiori, in sensing the reciprocal action of these changes. Then we can consider the interaction between the incident electron and the atom to be weak, and we can derive expressions by perturbation theory for the cross-sections for electron scattering and for excitation and ionization of the atom. This method is called the Born approximation, and it has been studied in detail (see [1-3]). The accuracy of the Born approximation falls with decreasing energy. Calculation of scattering cross sections at incident-electron energies of the order of the binding energy of the atomic electrons are of great practical interest. Here the velocity of the scattered electron does not differ substantially from those of the atomic electrons, and we cannot generally treat its interaction with the atom as a perturbation. Hence the Born approximation gives results that are correct only in order of magnitude.

A number of methods have been developed and are being applied for calculations in this energy range: the close-coupling method, the static approximation, the polarized-orbital method, the variation principles of Kohn, Hulthén, and Rubinow, and their modifications. They are all more laborious than the Born approximation. Most of the calculations have been done by the close-coupling method, and a fraction of the other methods are variants of it. For example, the static approximation implies that one keeps in the close-coupling

method only one equation that corresponds to scattering by the atom in its ground state. The distorted-wave method can be applied if the system of equations of the close-coupling method can be separated into two (or more) subsystems whose coupling with one another is so weak that we can account for it by first-order perturbation theory. However, with the development of computing technique, the need of using a special method in such cases has declined. Accordingly, the number of calculations that have been performed by the distorted-wave method has diminished. The polarized-orbital method resembles both in principle and results the use of pseudostates in the generalizations of the close-coupling method.

The atomic units $e = \hbar = m_e = 1$ are used in the formulas of this article.

2. THE CLOSE-COUPPING METHOD AND ITS RESULTS

When we treat the scattering of an electron by an N -electron atom with the total energy E , orbital angular momentum L , and spin angular momentum S , we must find totally antisymmetric solutions of the Schrödinger equation

$$(\mathcal{H} - E)\Psi = 0, \quad (1)$$

such that, as the coordinates of the one electron approach infinity, they will behave as

$$\Psi_j \sim \sum_{i=1}^N \frac{\psi_i}{r_{N+1}} \frac{1}{\sqrt{k_i}} (e^{-i[k_i r_{N+1} - (\pi l_i/2)]} \delta_{ij} - e^{i[k_i r_{N+1} - (\pi l_i/2)]} S_{ij}), \quad (2)$$

and this defines the scattering matrix S . The

$$\psi_i = \sum_{M_i, m_i, M_{i-1}, \mu} (L_i L_i M_i m_i | LM) (S_{i-1/2} M_{i-1} \mu | SM_i) \times \psi_{ia}(X_1, \dots, X_N) \chi_{1/2, \mu}(\sigma_{N+1}) Y_{l_i m_i}(r_{N+1}) \quad (3)$$

denote the linear combinations of products of the atomic functions ψ_{ia} , of the spin functions of the scattered electron χ , and of the spherical functions Y , which depend on its direction, with the Clebsch-Gordan coefficients

that correspond to the angular momenta L and S that are being considered. One must sum in the boundary condition (2) over the ground state of the atom and those excited states that can be excited at the given energy E .

The exact solutions of Eq. (1) are unknown. Since it is a differential equation in the partial derivatives of $3(N+1)$ variables, one also cannot directly integrate it numerically. At low energies, the Born approximation gives insufficiently exact results. Hence one uses direct methods of calculation in which the Hamiltonian H is replaced with another one whose solutions can be found by numerical integration, such that the latter solutions must approximate the exact solutions of Eq. (1).

The fact that the boundary conditions (2) contain the atomic wave functions substantially restricts the freedom of choice of the approximate methods. Hence, the solutions of the approximate equation must behave at infinity in the same form as (2), while differing from the exact solution only in the elements of the S matrix.

In view of this, one chooses in the so-called close-coupling method^[1, 4-10] a form for the approximate wave function that is as close as possible to the form of the boundary condition (2):

$$\Psi^t = A \sum_i \psi_i \frac{F_i(r_{N+1})}{r_{N+1}}. \quad (4)$$

In Eq. (4), the operator A antisymmetrizes the function, and the F_i 's are the (as yet) arbitrary radial functions of the scattered electron.

This method is a generalization to the problem of a continuous spectrum of the Hartree-Fock method that is used for calculating discrete spectra. Massey and Mohr^[11] first used it in 1932 to study electron-atom collisions.

We can derive the system of equations for the functions F_i most simply by substituting Eq. (4) into Eq. (1), multiplying successively by each of the functions ψ_j^* contained in the summation of (4), and integrating over all the variables except r_{N+1} .

$$\int \psi_j^* (\mathcal{H} - E) \Psi^t dX_1 \dots dX_N d\Omega_{N+1} = 0. \quad (5)$$

We can derive the very same system by using the expression (4) in the variation principle for the scattering matrix, and requiring that the difference between the approximate and exact S -matrices should be quadratically small in comparison with the difference between the approximate and exact functions. If Eq. (4) contained no antisymmetrization operator, we would get a system of ordinary second-order differential equations, and there would be just as many of them as there are of the functions F_i . The antisymmetrization somewhat complicates the situation, and the equations obtained are not differential, but integrodifferential equations:

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{L_j(L_j+1)}{r^2} \right] F_j(r) = 2 \sum_i \left(V_{ji}(r) F_i(r) + \int_0^\infty W_{ji}(r, r') F_i(r') dr' \right). \quad (6)$$

In the exchange terms, the functions F_i to be calculated enter into the integrands.

We can write Eqs. (5) and (6) in more general form. Following Feshbach,^[12] we shall introduce the projection operator Q_t , which isolates from any function that has the same arguments as Ψ^t the component that is orthogonal to all the functions of the form (4) with arbitrary

F_i 's. If we denote $P_t = 1 - Q_t$, we get the system (5) in the form

$$(P_t \mathcal{H} P_t - E) P_t \Psi^t = 0. \quad (7)$$

We see that the equations of the close-coupling approximation differ from the exact equation (1) by replacing H by $P_t H P_t$, or the original Hamiltonian multiplied on both sides by the projection operator P_t .

The different approximations and their operators P_t differ in the number and choice of the functions ψ_i in the summation of (4). The boundary conditions (2) can be satisfied only if the summation (4) contains all states that can be excited at the given energy. Hence, the crudest, yet not contradictory, approximation of the close-coupling method consists in accounting for all these states, which correspond to the so-called open channels, and neglecting all the rest. We shall denote the operators P_t and Q_t of this approximation by P and Q . We can improve the approximation by including in the summation (4) states whose excitation is energetically impossible (closed channels). As we increase the number of functions corresponding to closed channels, we can expect the accuracy of the approximation to increase monotonically, since the operators P_t will define an ever larger, and the Q_t an ever smaller part of the function space:

$$P < P_t < 1, \quad Q > Q_t > 0, \quad (8)$$

and the equation (7) will approach the exact (1).

The method is directly applicable only at energies below the ionization threshold as long as the number of excited states is finite, and the number of equations in the system (6) is also finite.

Three types of results have thus far been obtained by using the close-coupling method. First, effective scattering and excitation cross sections have been calculated by numerical integration of the system (6) on a computer. The wave functions obtained here have been used in a number of cases for finding photoionization cross sections. Second, since the Eqs. (6) are approximate, people have studied how a change of the number of functions included in the summation (4) affects the results, and values have been found here that vary monotonically.^[13-15] An example is the scattering phase, which can only increase with increasing number of terms in Ψ^t . Hence the calculated phase is always smaller than the exact value. Third, the system (6) permits one to draw qualitative conclusions on the behavior of the cross sections with varying energy. Formulas have been derived that describe the behavior of the cross-sections near the thresholds of the different channels, when one or several of the k_j are small. This is a generalization of the method of the scattering length and the effective radius for the many-channel problem, with account taken of the polarizability of the atom and other long-range forces.^[16-23]

We shall take up in greater detail the question of what has been thus far calculated by the close-coupling method. The Table shows the atoms and approximations for which calculations have been performed. The Table is orientational, to give a general picture of what has been calculated, when, and how, and where published. Only calculations are listed that account for close-coupling of at least two states and for exchange. Calculations are not listed that have used the polarized-orbital, distorted-wave, or Born approximations. The Table also includes

Atom	Year	Coupled atomic states	References
H	1962	$1s-2s-2p$	34-31
	1965	$1s-30$ Correlations	32
	1966	$1s-2s-2p-16$ Correlation	33
	1966	$1s-2s-2p-3s-3p-3d$	34, 35
	1967	$1s-2s-2p-20$ Correlations	36
	1969	$1s-2s-2p-2\bar{p}$	37
	1970	$1s-2s-2p-3s-3\bar{p}-3\bar{d}$	38, 39
	1970	$1s-2s-2p-3s-3\bar{p}, E > E_{ion}$	40
	1974	$1s-2s-2p, E > E_{ion}$	41
	1974	$1s-2s-2p-3d-3s-4s-5s-3\bar{p}-4\bar{p}-5\bar{p}-4\bar{d}, E > E_{ion}$	42
He ⁺	1964	$1s-2s-2p$	43, 44
	1964	$1s-2s-2p-3s-3p$	45
	1966	$1s-2s-2p-18$ Correlations	33
	1967	$1s-2s-2p-3s-3p-3d$	46
	1969	$1s-2s-2p-20$ Correlations	47
He	1966	$1s^2 1S-1s2s^2 1S-1s2p^2 1P$	48-50
	1966	$1s^2 1S-1s2s^2 1S-1s3s^2 3S$	53
	1967	$1s^2 1S-32$ Correlations	54
Li ⁺	1970	$1s^2 1S-1s2s^2 1S-1s2p^2 1P$	55
Li	1964	$2s-2p$	56-59
	1967	$2s-2p-3s$	63
	1969	$2s-2p-3d$	64
Be ⁺	1967	$2s-2p$	65
C ³⁺	1972	$1s^2 2s-1s^2 2p$	66
N ⁴⁺	1966	$1s^2 2s-1s^2 2p$	67
Be	1974	$1s^2 2s^2 1S-1s^2 2s2p^2 1P$	68
C ²⁺	1972	$1s^2 2s^2 1S-1s^2 2s2p^2 1P$	69
N ³⁺	1973	$1s^2 2s^2 1S-1s^2 2s2p^2 1P$	70
N ²⁺	1973	$1s^2 2s^2 2p^2 1P-1s^2 2s2p^2 1P(1D-1S)$	71
C	1967	$1s^2 2s^2 2p^2 1P(1D-1S)$	40, 71-73
N ⁺	1966	$1s^2 2s^2 2p^2 1P(1D-1S)$	49, 74, 75
	1970	$1s^2 2s^2 2p^2 1P-1s^2 2s2p^2 1P(1D-1S)$	76
	1974	$(1s^2 2s^2 2p^2 + 1s^2 2p^4)(1P-1D-1S)-1s^2 2s2p^2 1P(1D^3S-1P)$	77
O ²⁺	1968	$1s^2 2s^2 2p^2 1P(1D-1S)$	49, 70, 72, 73
	1969	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s2p^2 1P 6S$	78
	1969	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s2p^2 1P 3D$	78
N	1967	$1s^2 2s^2 2p^2 1P(1D-1S)$	49, 71-73
	1973	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s2p^2 1P 4P$	70
	1973	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s2p^2 1P 4P$	70
O ⁺	1968	$1s^2 2s^2 2p^2 1P(1D-1S)$	72, 73
	1973	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s2p^2 1P 4P$	70
O	1967	$1s^2 2s^2 2p^2 1P(1D-1S)$	49, 72, 73, 79
	1973	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s^2 2p^2 3P$	70
	1973	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s^2 2p^2 3D$	70
	1974	$1s^2 2s^2 2p^2 1P(1D-1S)-1s^2 2s^2 2p^2 3s$	80
		$(3S-3D-3P)-1s^2 2s^2 2p^2 1P(1D-1S)(3S-3D-3P)$	80
Ne ⁺	1967	$1s^2 2s^2 2p^2 1P-1s^2 2s2p^2 1S$	49, 81
Ar ⁺	1967	$1s^2 2s^2 2p^2 3s^2 3p^2 1P-1s^2 2s^2 2p^2 3s^2 3p^2 1S$	49, 81
Na	1965	$3s-3p$	57-59
	1972	$3s-3p-3d-4s$	82-83
Mg ⁺	1967	$3s-3p-3d$	65
Mg	1970	$3s^2 1S-3s3p^2 1P$	68, 84, 85
K	1965	$4s-4p$	57, 58, 60, 61, 66
Ca ⁺	1968	$4s-4p-3d$	87, 88
Ca	1975	$4s^2 1S-4s4p^2 1P$	89
Sr	1975	$5s^2 1S-5s5p^2 1P$	89
Cs	1965	$6s-6p$	57, 58, 60, 61, 69
Ba	1975	$6s^2 1S-6s6p^2 1P$	89

calculations in which a fraction of the closed channels has been taken as a linear combination of a finite number of quadratically integrable correlation functions (the number of functions is indicated), together with calculations that use pseudostate functions (the symbols are superlined). If a less exact approximation was used simultaneously with a more exact one, or after it, only the more exact one is kept in the Table. The year indicates when the numerical results of the given approximation were first published. Most of the cases have treated elastic scattering and transitions between all of the states whose close-coupling was taken into account. If some states are closed at the given energy, the resonances in the cross-sections arising from them were studied.

We see from the Table that the first calculations by the close-coupling method were performed in the early sixties. The cross sections for elastic scattering and for excitation of the lowest levels of the hydrogen atom were treated in the approximations $1s-2s-2p$ and $1s-2s-2p-3s-3p-3d$ (the references are given in the Table). Then scattering was treated in an analogous way in the hydrogen-like ion He^+ , in the alkali-metal atoms Li, Na, K, and Cs, and in the helium atom. Figures 1-3 show the results for the cross sections for excitation of the $2p$ level of the hydrogen atom and for elastic scattering by Li and Na.

Scattering cross sections were subsequently calculated for C, N, and O, with account taken of close coupling between the three lowest states. These states have the same configuration of electrons $1s^2 2s^2 2p^1$, but they are distinguished by different values of L and S. In order of increasing energy, they are: $^3P-^1D-^1S$ for C and O, and $^4S-^2D-^2P$ for N. The scattering and excitation of the alkali-earth atoms Mg, Ca, Sr, and Ba have recently been calculated.

These calculations have been performed independently of one another on different computers. The computational programs for each group of atoms were written practically anew. Starting in 1968, a tendency has arisen to create universal programs that permit one to calculate the scattering by any atom or ion. [49, 66, 69, 92-96] Before calculating, one must only "indicate" to the computer the concrete atom and the states whose close coupling one wishes to take into account. These programs are of large dimensions (thousands of punched cards), and they have been written for powerful computers.

Let us now say a few words on how the computations are done in practice. The problem immediately arises for many-electron atoms of the approximate atomic wave functions and the corresponding energy values. Thus far, the Hartree-Fock self-consistent-field functions have usually been used. Numerically-tabulated functions [97-101] have been used in scattering calculations for the alkali and alkaline-earth elements. [55-60, 62, 68, 85, 86] In other programs, the radial parts of the atomic functions have often been approximated analytically by finite power series and Slater-type exponentials like

$$P(r) = \sum_{\alpha} C(\alpha) r^{l(\alpha)} e^{-\xi(\alpha)r}. \quad (9)$$

Experimental energies have often been introduced instead of the Hartree-Fock values in order to facilitate comparison of the results with experiment. It has been proposed in certain universal programs to use also the multiconfigurational wave functions, while again approximating their radial dependence in the form of (9).

One substitutes the atomic functions into Eqs. (3), (4), and (5), calculates the potentials $V_{ji}(r)$, and the kernel of the exchange integrals $W_{ji}(r, r')$ of the system (6). In order to integrate over the angles, the interaction of the electrons is expanded in terms of multipoles, and the corresponding angular integrals are expressed in terms of the Racah coefficients. [7] Thus the potentials are expressed in terms of one-dimensional integrals that contain the radial functions of the atomic electrons. The approximation (9) permits one to take these integrals and to derive analytical formulas for the potentials. If one uses tabulated radial functions, then the integrals

are calculated numerically. The kernels of the exchange integrals are expressed in terms of the radial functions of the atomic electrons $P_a(r)$ in the form

$$W_{ji}(r, r') = \sum_{a,b,\lambda} P_a(r) [A \gamma_{\lambda}(r, r') + B \delta_{\lambda,0}] P_b(r'), \quad (10)$$

where

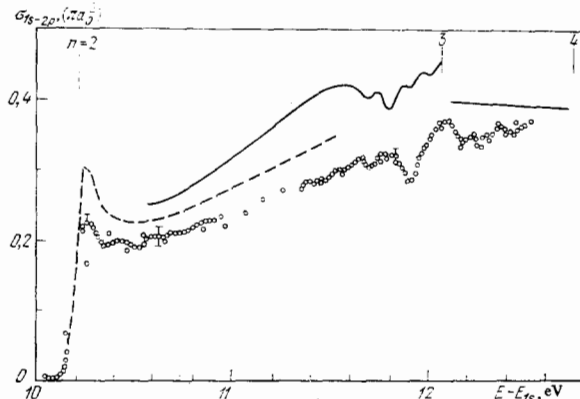


FIG. 1. Energy-dependence of the cross-section for excitation by electrons of the 2p level of the hydrogen atom. Solid curve—calculation in the 1s-2s-2p-3s-3p-3d approximation, [35] dotted curve—calculation in the 1s-2s-2p-2a-correlation approximation. [36] The given curves are averaged over an electron spectrum of width 0.07 eV. The experimental results are also given. [90]

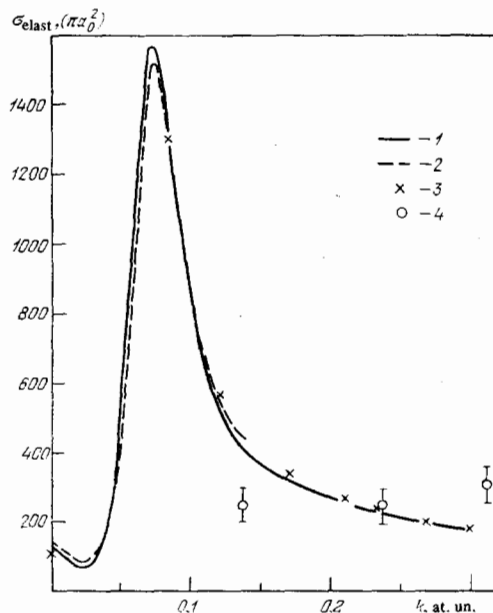


FIG. 2. Total elastic scattering cross-section of electrons by Li atoms in the 2s-2p-approximation. 1—Results of Sinfaillam and Nesbet [50] calculated by Nesbet's method, 2—results of Norcross, [61] 3—results of Karule, [58] 4—experiment. [91]

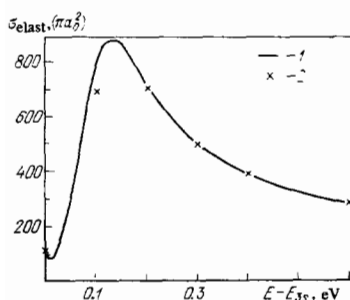


FIG. 3. Total elastic scattering cross-section of electrons by Na atoms in the 3s-3p approximation. 1—Results of Norcross, [61] 2—results of Karule. [58]

$$\gamma_{\lambda}(r, r') = \min \left(\frac{r^{\lambda}}{r^{\lambda+1} + 1}, \frac{r'^{\lambda}}{r'^{\lambda+1} + 1} \right), \quad (11)$$

and A and B are constants that depend on i, j, a, b, and λ .

Up to now, three methods have been used for numerical solution of the system of integrodifferential equations (6). The first calculations accounted for the exchange terms by iterations. However, the iteration process converges slowly, and sometimes even diverges.

Currently one generally uses the Drukarev-Marriott [102, 103] method. Here one takes account of the fact that the kernels of (10) are finite sums of products of functions of r and r', and one transforms (6) into a system of ordinary differential equations of higher order and a system of linear algebraic equations. The third method has been proposed in [9] and programmed in [69]. By using numerical integration formulas within the atom, the integrodifferential equations are converted into matrix equations. The matrices here are of large dimensions, and especially written subprograms are needed to work with them. The exchange terms vanish outside the atom, and the equations of the system (6) become differential equations.

The differential equations in all three methods are integrated numerically, usually with a variable integration increment. Here the initial conditions for the different linearly-independent solutions are

$$F_{iq}(r) \underset{r \rightarrow 0}{\sim} r^{l_i+1} \delta_{iq}. \quad (12)$$

The scattering matrix is determined by the boundary condition at infinity that is imposed on the linear combinations of the functions $F_{iq}(r)$:

$$\sum_q F_{iq}(r) c_{qj} \underset{r \rightarrow \infty}{\sim} \frac{1}{\sqrt{k_i}} \left[\sin \left(k_i r - \frac{\pi l_i}{2} \right) \delta_{ij} + \cos \left(k_i r - \frac{\pi l_i}{2} \right) K_{ij} \right], \quad (13)$$

$$S = (1 + iK)(1 - iK)^{-1}.$$

One can improve the boundary condition (13) in order to shorten the range for numerical integration. By using a multipole expansion of $V_{ji}(r)$ outside the atom, one introduces asymptotic formulas for the solutions of (6) at large r. These solutions have the form of (13), but coefficients in the form of inverse power expansions in r appear in front of the sine and cosine terms.

3. RESONANCES IN THE CROSS-SECTIONS AND EXTREMAL PROPERTIES OF THE CLOSE-COUPPLING METHOD

The close-coupling method has two important problems: calculating the resonances in the cross sections and the problem of the dependence of the accuracy of the calculations on the approximation being used. They prove to be interrelated.

A large number of resonances is found, both in the calculations and experimentally. [104, 105] One can see the resonances in scattering by the hydrogen atom in Figs. 1 and 4. Two causes of resonances are commonly found: either the potential has a peculiar form in one of the open channels (a well of sufficient depth and width lies beyond a rather broad barrier, and the electron being scattered is temporarily bound to it in an autoionization state), or the electron is bound in an autoionization state in one of the closed channels.

Resonances of the second type are called Feshbach resonances. Feshbach studied them, while writing (1) in the form of the system

$$P(\mathcal{H} - E)(P + Q)\Psi = 0, \quad (14)$$

$$Q(\mathcal{H} - E)(P + Q)\Psi = 0$$

and eliminating $Q\Psi$ from it. He obtained the equation^[12]

$$P(\mathcal{H} - E + W)P\Psi = 0, \quad (15)$$

$$W = P\mathcal{H}Q(Q(E - \mathcal{H})Q)^{-1}Q\mathcal{H}P,$$

Mathematically, this is equivalent to the Schrödinger equation (1), and it is convenient for various proofs, since in form it resembles (7). Equation (15) is less convenient for direct solution, since W , which is called the polarization (or optical) potential, contains the operator $[Q(\mathcal{H} - E)Q]^{-1}$, for which no explicit expression is known. The polarization potential depends on E , and it is responsible for the resonances. Since Q defines the channels that are closed at the given energy, the eigenvalues of the continuous spectrum of the operator $Q\mathcal{H}Q$ are always larger than E . If it also has discrete eigenvalues, they correspond to the autoionization states in the closed channels. Usually they are only slightly below the boundary of the continuous spectrum of $Q\mathcal{H}Q$, i.e., the threshold for excitation of states of the closed channels. When E is close to one of these eigenvalues, a large term arises in the polarization potential, and a resonance in the scattering cross sections. If the discrete eigenvalues are not too close to one another, the resonances have the Breit-Wigner form, while their widths are expressed in terms of the squares of the matrix elements $Q\mathcal{H}P$.

The various approximations of the close-coupling method correspond to substituting various approximate expressions for the polarization potential. We see upon comparing Eqs. (15) and (7) that accounting for close-coupling between only the open channels is equivalent to neglecting the polarization potential, and consequently, neglecting the resonances that it produces. The more accurate approximations are equivalent to replacing \mathcal{H} by $P_t\mathcal{H}P_t$, i.e., replacing the polarization potential by

$$W_t = P\mathcal{H}P_tQ[QP_t(E - \mathcal{H})P_tQ]^{-1}QP_t\mathcal{H}P, \quad (16)$$

whereby the approximate values of the energies of the resonances are obtained as the eigenvalues of $QP_t\mathcal{H}P_tQ$. Since $Q\mathcal{H}Q$ is bounded below by the operator, multiplying it on both sides by the projection operator P_t elevates all the eigenvalues. Hence, the energy values of the resonances calculated in the close-coupling approximation always prove to be above the exact values, and the cruder the approximation is, the higher they are. The energies of the resonances are depressed monotonically downward as the approximation is improved.

If E is below the energies of all the resonances, then the operator $Q(E - \mathcal{H})Q$ is negative, and all its eigenvalues and mean values are negative. Its inverse opera-

tor is also negative. Hence also the polarization potential proves to be negative:

$$W < 0, \quad (17)$$

This leads to attraction of the scattered electron toward the atom. The calculations in the approximation of the close-coupling method are equivalent to replacing W by the operator of (16), which also proves to be negative: $W_t < 0$. However, the projection operator P_t that enters into (16) has the result that the approximately-calculated attraction of the scattered electron toward the atom is always weaker than the actual value:

$$W < W_t, \quad (18)$$

This can be proved rigorously mathematically.^[15] The difference $W_t - W$ declines monotonically as the approximation is improved. In turn, this relationship causes a monotonic change in the scattering matrices and phases. Perturbation theory implies that, when the potential changes by δW , the phase and the K-matrix vary as

$$\delta\eta = -2 \int_0^\infty F\delta W F dr, \quad (19)$$

$$\delta K = -2 \int_0^\infty F^T \delta W F dr,$$

where the F 's are the solutions for the unchanged potential.

In both integrals, the sign of the integrand always agrees with that of the change in the potential. Hence $\delta\eta$ and δK have a sign opposite to that of δW . Therefore, the phase of the scattering and the K-matrix as calculated in the close-coupling approximation are smaller than the exact values, and they monotonically approach the exact values from below as the approximation is improved. This permits one to estimate directly from the calculations the choice of results that is more exact, and of closed channels that are most important to take into account. For example, in treating elastic scattering, the calculation is most exact and the states are most important for which the largest scattering phase is obtained. Of course, this holds only when the numerical integration has been done accurately enough. To speak of monotonic relationships, we assume that exact atomic wave functions are used for the open channels. If approximate atomic functions are used, the monotonic relationships also hold only approximately.

4. PROBLEMS AND GENERALIZATIONS

We shall treat below a number of the difficulties that one encounters in applying the close-coupling method, together with what people do to minimize or completely eliminate them. There are two fundamental difficulties. The first is that one can include in the summation of (4) only a small number of functions, and this restricts the accuracy of the approximation. The second is that the computational programs prove to be long, and they take much machine time. In particular, a great demand for machine time stems from the fact that one is calculating not individual numbers, but families of curves: the energy-dependence of the scattering matrices and the cross sections for each partial wave.

In principle, if we included in the summation of (4) all of the atomic wave functions, including an integration over the continuous spectrum, we would have an expansion in a complete system of functions, and we could get

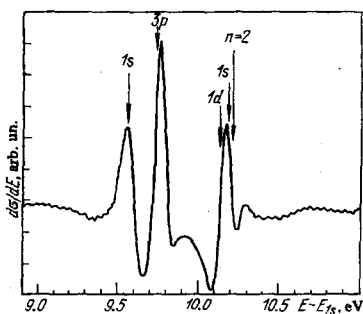


FIG. 4. Results of experimental study of the series of resonances in the elastic scattering cross-section of electrons by the hydrogen atom below the excitation threshold.^[106] The derivative of the cross-section with respect to the energy was measured. The arrows indicate the energy of the resonances that were calculated by the close-coupling method.

exact results. Unfortunately, in practice one can account for only a small number of discrete states. Hence one can treat only scattering by the lowest states, while one cannot at all calculate the ionization cross section without changing the method.

The finite number of functions also leads to a false qualitative behavior of the calculated cross sections. For example, as we know, an electron is attracted at large distances to a neutral atom in the ground state by the potential $-\alpha/2r^4$, where

$$\alpha = 2 \sum_i \frac{|\langle \psi_{ip} | \sum_{t=1}^N r_t | \psi_{n_0s} \rangle|^2}{E_i - E_{n_0s}} \quad (20)$$

is the polarizability of the atom. Therefore the elastic-scattering phase at small k^2 and $L \geq 1$ behaves according to the relationship:^[16]

$$\text{tg } \delta_L = \frac{\pi \alpha k^2}{(2L+3)(2L+1)(2L-1)}. \quad (21)$$

Scattering phases calculated by the close-coupling method at small energies also prove to be proportional to k^2 , but they have a coefficient as though one included only the same functions as in the summation of (4) when calculating the polarizability in the summation of (20). In particular, the calculated phases have only about 2/3 of their exact values for hydrogen in the $1s-2s-2p$ approximation for small k^2 and $L \geq 1$.

People try to diminish such difficulties by including in the summation of (4) other functions, which are called pseudostate functions, as well as the atomic functions. Since the character of such difficulties depends on the energy being considered, the type of pseudofunctions to be taken into account also changes with varying energy. As yet, the pseudofunctions have been used only for closed channels, while using atomic wave functions for the open channels, and the results preserve the extremal properties mentioned above.

Apart from a normalizing coefficient, one derives a pseudofunction that permits one to take account of the correct dipole polarizability by treating an atom in its ground state placed in an external electric field, and isolating from its wave function the part that is proportional to the external field. It satisfies the inhomogeneous differential equation

$$(\hat{\mathcal{H}}_{\text{at}} - E_{n_0s}) \psi_p = \sum_{t=1}^N r_t \psi_{n_0s}. \quad (22)$$

For hydrogen, its radial part is^[107, 108]

$$P_{2\bar{p}} = \text{const} \left(r^2 + \frac{r^4}{2} \right) e^{-r}. \quad (23)$$

The functions of pseudostates that give the dipole polarizability of the excited states and the quadrupole polarizability of the ground state of hydrogen,^[109-111] as well as the dipole polarizability^[80, 112] of He, Ne, Ar, N, and O, have been analogously calculated. Numerical scattering calculations with account taken of these pseudostates have been performed for H, He, and O.

The requirements for exact accounting for polarizability are relaxed with increasing energy at small angular momenta L . Matese and Oberoi^[39] have found that one gets scattering phases here that are large in magnitude, i.e., more exact, if one accounts for pseudofunctions of another type, such as will give low values of the energy of the ground and autoionization states of the H^- ion.

The situation again changes radically with further

increase of energy, especially above the ionization threshold. So many open channels arise that one cannot even include them all in the summation of (4) so as to satisfy the boundary conditions. For a long time, the close-coupling method was not used at all at such energies, since it was not known what to do in such a situation. Calculations have recently appeared in which the idea of pseudostates has again been used.^[40-42] Exact wave functions of the hydrogen atom were taken for all the discrete states among which transitions were being considered. Instead of the others, it was proposed to take functions that are orthogonal to the functions of the atomic states that were taken into exact account, but in other respects they were arbitrary. One creates from them linear combinations S_i , such that

$$\langle S_i | \hat{\mathcal{H}}_{\text{at}} | S_j \rangle = E_i \delta_{ij}, \quad \langle S_i | S_j \rangle = \delta_{ij}, \quad (24)$$

and treats them by the close-coupling method, as though the atom had states with the functions S_i and energies E_i . Here one hopes to take approximate account with a small number of pseudostates of the transitions to the infinitely numerous unconsidered atomic states. The excitation of the $2s$ and $2p$ levels in the $1s-2s-2p-3s-3p$ approximation, and ionization in the $1s-2s-2p$ approximation were calculated in this way for hydrogen above the ionization threshold.^[41] For calculating the ionization cross sections, one first calculates the formal excitation cross-sections of the $2\bar{s}$ and $2\bar{p}$ pseudostates, and then multiplies each of them by the weighting coefficient of the continuous spectrum in the corresponding pseudofunction, and adds the results:

$$\sigma_{\text{ion}} = \left(1 - \sum_{n=1}^{\infty} \langle 2\bar{s} | ns \rangle^2 \right) \sigma_{1s, 2s} + \left(1 - \sum_{n=2}^{\infty} \langle 2\bar{p} | np \rangle^2 \right) \sigma_{1s, 2\bar{p}}. \quad (25)$$

The weighting coefficients are written in terms of sums over the discrete states to facilitate their direct numerical calculation. The ionization cross sections obtained in the calculation agree amazingly well with the experimental values.

Besides using pseudostates, one can improve the accuracy of calculation by other methods. In order to satisfy the boundary conditions (2), only the contribution of the open channels $P\Psi$ must have the form of (4). The contribution of the closed channels $Q\Psi$ can be accounted for in a different form, including a linear combination of a finite number of assigned functions η_j :

$$\Psi^i = A \sum_i \psi_i \frac{F_i(rN+1)}{rN+1} + \sum_{j=1}^m c_j \eta_j. \quad (26)$$

One obtains a system of integrodifferential equations for calculating the functions F_i , and the following system of algebraic equations for the coefficients c_j :

$$(\eta_j | \hat{\mathcal{H}} - E | \Psi^i) = 0. \quad (27)$$

One can take the number of the functions η_j , which are called correlation functions, to be rather large, and include among their arguments the relative distances of the electrons. The appropriate numerical calculations have been performed for hydrogen and helium.

In the studied method, only the closed channels are taken into account with the finite system of linear algebraic equations of (27). One can also transform the integration of the equations for the functions of the open channels within the atom into the solution of a system of algebraic equations. One of these methods is called the R -matrix method,^[112] and it is devised in the form of a

universal program for calculating the scattering by an arbitrary atom.^[96] One takes the test function in the form of (26). The distance a is taken to be larger than the dimensions of the atom, so that outside it one can consider all of the atomic functions to be practically zero:

$$\psi_i = \eta_j = 0, \quad \text{if } r \geq a. \quad (28)$$

Then when $r \geq a$, the functions F_i satisfy the ordinary differential equations of the system (6) without the exchange terms

$$W_{ji}(r, r') = 0, \quad (29)$$

with potentials that contain only several negative powers:

$$V_{ji}(r) = \sum_{\lambda} \frac{d_{ji}^{\lambda}}{r^{\lambda+1}}, \quad (30)$$

Here the d_{ji}^{λ} are the multipole matrix elements. The solutions of these equations must be adjusted to the solutions within the atom at $r = a$. The adjustment condition is written in the form

$$F_i(a) = \sum_j R_{ij} \left(a \frac{dF_j(r)}{dr} - b F_j(r) \right) \Big|_{r=a}, \quad (31)$$

where b is an arbitrary constant. We have chosen the form of (31) for this condition because it has long been found in the theory of nuclear reactions how the R-matrix is expressed in terms of the solution of the following auxiliary problem.

Let E_q and $F_{iq}(q)$ be discrete eigenvalues and eigenfunctions such that

$$(\Psi_q | \mathcal{H} | \Psi_q) = E_q \delta_{qq'}, \quad (\Psi_q | \Psi_{q'}) = \delta_{qq'} \quad (32)$$

under the condition

$$a \frac{dF_{iq}(r)}{dr} \Big|_{r=a} = b F_{iq}(a), \quad (33)$$

Here the Ψ_q 's contain $F_{iq}(r)$ in the form of (26), and the integration over r in the matrix elements of (32) is performed only in the finite interval from 0 to a .

Then, according to^[113, 114],

$$R_{ij} = \frac{1}{2a} \sum_q \frac{F_{iq}(a) F_{jq}(a)}{E_q - E}. \quad (34)$$

Both of the conditions (31) and (33) contain the arbitrary constant b , and the matrix R will depend on it, yet the final results, the scattering matrix and the cross sections, need not depend on it.

One can obtain approximate values of $F_{iq}(a)$ and E_q by substituting into (26) and (32) F_i in the form of linear combinations of a finite number of functions that are mutually orthogonal in the interval from 0 to a , which all obey the boundary condition (33). Consequently the calculations within the atom are reduced to calculating the matrix elements between these functions, and then finding the eigenvalues and the eigenvectors of the problem (32). The important thing is that one need not do this for each energy E , but only once, which substantially economizes on machine time. Then one calculates the R-matrix by Eq. (34) for each energy E , and using (31) as the initial condition, one numerically integrates the system (6) with the potentials of (30) and (29) from a to r values so large that the asymptotic expansions of the solutions are applicable, and one can find the scattering matrix from (13). Modifications of the R-matrix method have been proposed in^[115-117].

Now let us examine what type of equation one can derive by applying the fundamental principle of the close-coupling method: replacing the exact Schrödinger equation (1) by an approximate but simpler equation such that its solutions will be close, and will satisfy the boundary conditions of the same type (2) at large distances. One can do this only when an important condition is satisfied: the approximate equation has nontrivial solutions at all energies of the continuous spectrum of the exact equation, while the numbers of linearly independent solutions of the two equations must coincide. If one takes account of close-coupling between all the channels that are open at the given energy, then the system (6) satisfies this requirement. This is ensured by the differential operator on the left-hand side of (6). Both (1) and (6) possess a continuous spectrum, because in both cases they are differential equations: (1) involving partial derivatives, while (6) is a system of ordinary differential equations. The requirement is also satisfied when we take account of part of the closed channels in the form of the linear combination (26) of assigned quadratically-integrable functions, since one calculates the part of the wave function that corresponds to the open channels by solving the differential equations. One can simplify the form of the approximate function even further by representing the part that corresponds to the open channels, i.e., $P\Psi$, as a linear combination of the assigned functions. However, this violates the requirement for existence of nontrivial solutions for all energies of the continuous spectrum. Serious difficulties consequently arise. Nevertheless, this method seems tempting, since it eliminates the laborious and not very accurate procedure of numerical integration of the system of differential equations. Let us study this problem in greater detail.

Let us assume a problem with n open channels. We can draw up the approximate function in the form of the linear combination

$$\Psi^t = \varphi\alpha + \eta\beta. \quad (35)$$

Here φ is a row of $2n$ functions: we shall denote the first n functions as S , and the subsequent ones as C . Then as $r \rightarrow \infty$,

$$\begin{aligned} S &\sim \frac{1}{r} \frac{1}{\sqrt{k}} \sin \left(kr - \frac{\pi l}{2} \right) \psi_l, \\ C &\sim \frac{1}{r} \frac{1}{\sqrt{k}} \cos \left(kr - \frac{\pi l}{2} \right) \psi_l; \end{aligned} \quad (36)$$

We denote by η a row of m functions taken from the complete system of quadratically integrable functions, and the number m can be varied here. We can conveniently classify the coefficients α into two groups α_s and α_c ; α , α_s , α_c , and β are matrices having $2n$, n , n , and m rows, respectively, while each column pertains to its own linearly-independent solution, the number of which equals the number of open channels n .

We can find the equations for α and β in a way analogous to the way that (5) and (6) were derived. The action of the operator $\mathcal{H} - E$ on Ψ^t and the requirement of orthogonality of the result with respect to all the components in (35) of φ and η gives

$$(\varphi | \mathcal{H} - E | \Psi^t) = 0, \quad (\eta | \mathcal{H} - E | \Psi^t) = 0. \quad (37)$$

The following system of $2n + m$ equations arises:

$$\begin{aligned} \alpha_{sq}\alpha + \alpha_{cq}\eta &= 0, \\ \alpha_{sq}\alpha + \alpha_{cq}\eta &= 0, \end{aligned} \quad (38)$$

in which we have introduced the matrix notation:

$$\left. \begin{aligned} \mathcal{M}_{\varphi\varphi} &= (\varphi | \mathcal{H} - E | \varphi), & 2n \times 2n, \\ \mathcal{M}_{\varphi\eta} &= (\varphi | \mathcal{H} - E | \eta), & 2n \times m, \\ \mathcal{M}_{\eta\varphi} &= (\eta | \mathcal{H} - E | \varphi) = \mathcal{M}_{\varphi\eta}^T, & m \times 2n, \\ \mathcal{M}_{\eta\eta} &= (\eta | \mathcal{H} - E | \eta), & m \times m. \end{aligned} \right\} \quad (39)$$

The system (38) has a nontrivial solution only if its determinant is zero. For the assigned functions φ and η , this condition is satisfied only at discrete values of the energy. We must have $n > 1$ solutions above the excitation threshold. They exist only if the rank of the system (38) of $2n + m$ equations is $n + m$. This means that all the determinants of order greater than $n + m$ must vanish. One usually cannot satisfy simultaneously all these conditions and directly apply the system (38).

On the other hand, the quantity $\Psi - S - CK$, where Ψ is the exact solution and K is the exact reactance matrix, must approach zero at infinity as $O(r^{-2})$. Hence one can expand it in a power series in η , and when m is great enough, there are grounds for considering the approximation (35) to be rather accurate, and to expect that the accuracy will increase with increasing m .

We can conveniently transform the system (38) into a form that contains only the coefficients α of the open channels. This resembles the introduction of the polarization potential that transforms the exact Schrödinger equation (1) into Eq. (15), which defines only part of the open channels of the wave function $P\Psi$. From the second equation of (38), let us express β in terms of α :

$$\beta = -\mathcal{M}_{\eta\eta}^{-1} \mathcal{M}_{\eta\varphi} \alpha. \quad (40)$$

Substitution of (40) into (38) gives the system of $2n$ equations

$$M \cdot \alpha = 0, \quad (41)$$

$$M = \mathcal{M}_{\varphi\varphi} - \mathcal{M}_{\varphi\eta} \mathcal{M}_{\eta\eta}^{-1} \mathcal{M}_{\eta\varphi}. \quad (42)$$

We can conveniently separate the $2n \times 2n$ matrix M into four $n \times n$ matrices:

$$M = \begin{pmatrix} M_{ss} & M_{sc} \\ M_{cs} & M_{cc} \end{pmatrix} \quad (43)$$

and write (41) in the form

$$\begin{aligned} M_{ss} \alpha_s + M_{sc} \alpha_c &= 0, \\ M_{cs} \alpha_s + M_{cc} \alpha_c &= 0. \end{aligned} \quad (44)$$

The system (44) consists of $2n$ equations. It must have n nontrivial solutions. Hence its rank also must be n , and thus half of its equations are linearly independent, while the rest are linear combinations of them.

When $\alpha_s = 1$, according to (13), $K = \alpha_c$, and at large r ,

$$\Psi^t \sim S + CK. \quad (45)$$

In the general case, $K = \alpha_c \alpha_s^{-1}$. We can calculate the reactance matrix both from the first n equations of system (44)

$$K = -M_{sc}^{-1} M_{ss}, \quad (46)$$

and from the subsequent ones

$$K = -M_{cc}^{-1} M_{cs} \quad (47)$$

under the condition that the matrices M_{sc}^{-1} and M_{cc}^{-1} exist.

In the limit as $m \rightarrow \infty$, the rank of the system (44) is always n , and the two results (46) and (47) coincide.

For finite m , the determinant of the system (44) usually differs from zero, and Eqs. (44) are incompatible. This implies that the values from (46) and (47) will differ, and problems arise as to which of them is better, and whether one cannot find K more exactly by somehow

taking account of all of the equations of (44). Moreover, the approximate K -matrices calculated by Eqs. (46) and (47) for finite m often prove to be slightly asymmetrical, whereas the exact K -matrix is strictly symmetrical by the principle of detailed balancing.

One can improve the accuracy by using variation principles,^[118] in particular, those of Kohn (48), or Rubinow (49):

$$K = \text{St} [K^t - 2(\Psi^t | \mathcal{H} - E | \Psi^t)], \quad (48)$$

$$K^{-1} = \text{St} [K^{-1} - 2(\Psi^t | \mathcal{H} - E | \Psi^t)]. \quad (49)$$

The condition of a steady state implies that, if we substitute into (48) or (49) inexact wave functions Ψ^t with inexact K^t , we shall get results having quadratically small errors as compared with the error in Ψ^t . If we use (47) as the approximate value of K^t , while choosing Ψ^t in the form of (35) with $\alpha_s = 1$, $\alpha_c = K_t$, calculate β by Eq. (40), and substitute K^t and Ψ^t into (48), with account taken of

$$M_{sc} - M_{cs}^T = \frac{1}{2} \quad (50)$$

we get

$$K = -2[M_{ss} - M_{cs}^T M_{cc}^{-1} M_{cs}]. \quad (51)$$

By using analogously (46) and (49), we find

$$K^{-1} = 2[M_{cc} - M_{cs}^T M_{ss}^{-1} M_{cs}]. \quad (52)$$

These expressions give a symmetric K -matrix. The currently most accurate phase calculations of $e - H$ scattering have used Eq. (51). Schwartz^[119] calculated them for $L = 0$ in 1961. He used for η functions in the Hylleraas form

$$e^{-\kappa(r_1+r_2)} r_1^{l_1} r_2^{l_2} e^{i\mathbf{r}_1 \cdot \mathbf{r}_2 / R}, \quad (53)$$

Armstead^[120] analogously calculated the phases for $L = 1$ in 1968.

For a long time, such methods were not applied to more complex processes, mainly because in Schwartz's calculations the phase proved to be unstable with respect to the coefficient κ in the exponential of (53). The results were very similar at each energy for most of the κ values that Schwartz used, but they strongly differed for certain κ . He ignored the latter cases, while he took as the final result for each energy the mean phase for all of the rest of the κ values. This gave the impression that one generally cannot use variation methods to treat inelastic processes, where one calculates not a simple number (the phase), but matrices. Schwartz explained the instability with the idea that the determinant of the matrix $M_{\eta\eta}$ in Eq. (42) vanishes for certain values of κ .

In 1968, Nesbet^[121, 122] pointed out that this explanation is not fully justified, since the matrix $M_{\eta\eta}^{-1}$ gives rise to a singularity of the same form in all elements of the M -matrix, and with coefficients such that in (51) these singularities ultimately vanish. He pointed out that in Eq. (51) the K -matrix has a singularity at κ values such that $\text{Det } M_{cc} = 0$. Near these κ values, it is more sensitive to errors occurring specifically in the elements of the M_{cc} matrix. Vice versa, K^{-1} as calculated by Eq. (52) is more sensitive to errors in M_{ss} in the regions where $|\text{Det } M_{ss}|$ is small. Nesbet proposed comparing the determinants, and if

$$\left| \frac{\text{Det } M_{cc}}{\text{Det } M_{ss}} \right| \gg 1, \quad (54)$$

then we use (51). In the converse case, we first calculate K^{-1} by (52), and then by inverting it, we get K .

In 1971, Seiler et al.^[31] tested this method by calculating $e-H$ scattering. They took the test function in the form (4) in the close-coupling approximation of the $1s-2s-2p$ states. They used for F_i therein linear combinations of Bessel functions with half-integral indices (which corresponds to φ in (35)), and of functions $r^k e^{-\kappa r}$ having different values of k and κ (which corresponds to η in (35)). This choice of test function reduces to solving the equations of the close-coupling approximation of the $1s-2s-2p$ states by Nesbet's method. The results are close to those of numerical integration,^[24-30] while the calculation time is substantially shorter. Hence, one can use Nesbet's method directly for solving the equations of the close-coupling approximation. The results of the corresponding calculations^[31, 50, 51, 96] have been published for electron scattering by the atoms H, He, Li, Na, K, C, N, and O. We see from Fig. 2 how the elastic electron scattering cross-sections of Li calculated by Nesbet's method agree with the cross-sections obtained by numerical integration of the close-coupling equations.

Other variants of the method have also been proposed.^[123-125] We can see the potentiality and desirability of improving it from the following simple considerations. The K -matrix is block diagonal because of the conservation laws. Each block has its own set of values of conserved quantities. We can calculate any block separately by making up the function (35) from terms that correspond to definite values of the conserved quantities. We can also treat several blocks jointly by using in Eq. (35) a basis composed of all the functions that had been used in calculating the same blocks individually. Then the matrices M_{ss} , M_{sc} , M_{cs} , and M_{cc} are also block diagonal, and they are composed of matrices obtained by independent calculation of each block. The left-hand side of the criterion (54) will be the product of the left-hand sides obtained in the independent calculations, since the determinant of a block diagonal matrix is the product of the determinants of the diagonal blocks. If the relationship (54) is satisfied for all the blocks, it is also satisfied in their joint calculation, and in this case one always uses Eq. (51), and the results of separate and joint calculations agree. An analogous agreement occurs when none of the blocks satisfies (54). In the rest of the cases, part of the blocks will be calculated by (51), and the other part by (52). In the joint calculation, all of the blocks will be calculated by one of the formulas (51) or (52), depending on whether (54) is satisfied. This means that one will use the formula that is the best in the "geometric mean" over the blocks being treated. Certain blocks will be treated jointly by the one formula, but by the other one when treated separately. In fact, one expects a strong deviation of the results only in the chance coincidence when simultaneously the ratio in (54) is very large for one block, and (52) is explicitly inapplicable to it, while the ratio is very small for the other one, and (51) is inapplicable. However, we see from this that the method has elements of arbitrariness. The choice of the criterion (54) also is not rigorous. It is actually evident only that (51) is inapplicable for very small ratios in (54), and (52) for very large ratios. The requirement that one should change the formula when the determinants are exactly equal has been imposed arbitrarily. Finally, one can also use other variation principles instead of (48) and (49).

As an optimal variant, Nesbet and Oberoi^[125] have proposed that one should continuously change the varia-

tional principle applied as the matrix M varies, so that a criterion of the type of (54) should be satisfied as well as possible, while nonphysical singularities should not arise at all. For this purpose, one selects a unitary transformation U such that

a) it transforms the matrix M into an upper triangular matrix (with only zeroes below the main diagonal):

$$M' = U^* M U, \quad (55)$$

b) the diagonal elements in M' lie in order of increasing absolute value.

It is convenient to separate both matrices U and M' into four $n \times n$ matrices

$$U = \begin{vmatrix} U_{s0} & U_{s1} \\ U_{c0} & U_{c1} \end{vmatrix}, \quad M' = \begin{vmatrix} M'_{00} & M'_{01} \\ M'_{10} & M'_{11} \end{vmatrix}, \quad (56)$$

and to denote the first n of the $2n$ functions $\varphi' = \varphi U$ as φ'_0 , and the next n as φ'_1 .

The boundary condition (45) is replaced by

$$\Psi \sim \varphi'_0 + \varphi'_1 K' \quad (57)$$

and this defines the matrix K' . We can express the reactance matrix in terms of U and K' :

$$K = (U_{c0} + U_{c1} K') (U_{s0} + U_{s1} K')^{-1}. \quad (58)$$

A Kohn-type variational principle has been carried out in^[125] for K' . In the final result,

$$K' = -M'_{01}^{-1} M'_{00} \quad (59)$$

has only one term $M'_{10} = 0$ owing to the triangularity of the matrix M' , and the second term vanishes analogously to the second term in Eq. (51) when $M_{cs} = 0$. It has been shown that M'_{01}^{-1} exists, and hence, the relationship (59) gives rise to no nonphysical singularities. The arrangement of the diagonal elements of M' in increasing order leads to the lowest possible ratio $|\text{Det } M'_{00} / \text{Det } M'_{11}|$.

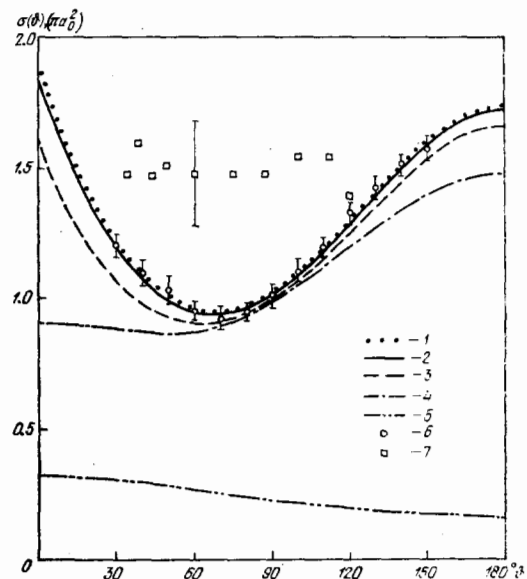


FIG. 5. Differential elastic scattering cross-sections of hydrogen atoms at $E - E_{1s} = 3.4 \text{ eV} \approx 0.125$ atomic units. 1—Variational calculations (the s, p, and d phases were taken from [32, 119, 120], respectively); 2—the $1s-2s-2p-2\bar{p}$ approximation; [37] 3—the $1s-2s-2p$ approximation; the stated approximations were used for the lower partial waves having angular momenta $L \leq 2$; the scattering phases for $L \geq 3$ were calculated by Eq. (21); 4—the static approximation; 5—the Born approximations; 6—experimental results of Williams; [126] 7—experimental results of Gilbody et al. [127] at 3.8 eV in 1961.

which indicates an optimal choice of the variational principle.

5. CONCLUSION

To summarize the presented material, one can say that elastic and inelastic electron-scattering cross sections for many atoms and ions have been calculated by the close-coupling method since the early sixties. Qualitative features of the cross sections have also been studied, including resonances. The calculational methods have been refined. The experimental technique and accuracy have simultaneously risen. Consequently the agreement of experimental and calculated data has substantially improved. As an example, Fig. 5 gives the absolute differential elastic electron-scattering cross sections of hydrogen atoms measured by Williams in 1974.^[126] The experimental errors that he indicated are appreciably smaller than the differences between the results of the different approximations of the close-coupling method. The experimental data practically coincide with both the calculations that used pseudofunctions that take account of the polarization of the atom, and with those that used correlation functions for the closed channels, and with the variational calculations. The results of the static approximation and the close-coupling approximation with only the $1s-2s-2p$ states lie outside the limits of experimental error. We note that the curves are not perpendicular to the axis of ordinates for small θ , as they are often extrapolated in experimental studies. This behavior of the cross sections is due to the polarizational attraction of $-\alpha/2r^4$ between the electrons and atoms.^[126] Figure 5 shows also the result of the Born approximation. We can see its evident unsuitability at such a low energy.

In conclusion, I wish to thank R. Kh. Propin for a stimulating discussion.

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