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Matrix Variational Method for Electron-Atom Scattering*

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Computational and data-handling algorithms are given for a matrix variational method designed for a broad class of problems in the quantum theory of electron–atom scattering. As implemented, the method is applicable to low energy elastic or inelastic electron scattering by a neutral atom of arbitrary shell structure.

1. INTRODUCTION

This paper presents previously unpublished details of a general method for quantum mechanical computation of the effects of electron scattering by target atoms containing more than one electron. The method to be described is applicable to low energy scattering by an atom of arbitrary shell structure, where several target states may be coupled by inelastic collisions. Several innovations are involved in this work, which seeks to extend matrix variational methods that have been successful in bound–state problems to the more difficult area of electron scattering.

The method presented here has developed in part from exploratory studies by Harris and Michels [1]. Aspects of the formalism and computational algorithms have been published separately [2–4]. Since the formalism has evolved in the course of implementation, an outline of the most current version will be given here in Section 2.

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A detailed critique of this method, and comparison with other approaches, will be published elsewhere [5]. For atoms beyond hydrogen, the most widely applicable method for low energy scattering is the *close coupling* method, recently reviewed by several authors [6]. For elastic scattering, physical effects of the response of the target atom to the scattered electron have been taken into account by the *polarized orbital* method [7]. Recently, the physical arguments behind the polarized orbital method have been put into the context of an *ab initio* method expressed in terms of coupled Green's functions [8]. In specific applications, the present method has been found to be competitive with the best results reported for these alternative methods. Implemented as described here, it has the advantage of very general applicability with no changes in computer programs.

The algorithms described here are of two kinds: arithmetic and data handling. A full description of the very complex and general procedures involved would be impossible without including data handling algorithms. Their planning and organization is as important to successful implementation of the method as is the analysis of purely arithmetic aspects.

The main body of this paper, Section 3, gives details of the various algorithms that have been implemented in a current computer version of the method. References to results obtained in applications to date are given in Section 4, together with some comments on limitations of the formalism or of the present implementation.

2. VARIATIONAL METHOD

Scattering of an electron by an N-electron atom can be described by a stationary state Schrödinger wave function constructed in the form

$$\Psi = \sum_p \mathcal{A}\Theta_p\psi_p + \sum_\mu \Phi_\mu c_\mu \,. \tag{1}$$

Here Θ_p is a normalized N-electron target atom wave function for a stationary state corresponding to open scattering channel p; ψ_p is the one-electron *open-channel orbital* wave function for channel p, with angular momentum l_p and wave-vector of magnitude k_p (asymptotic kinetic energy $\frac{1}{2}k_p{}^2$ in Hartree atomic units); Φ_μ is one of an assumed orthonormal set of $N+1$-electron Slater determinants. The quadratically integrable function

$$\Psi_H = \sum_\mu \Phi_\mu c_\mu \tag{2}$$

is the *Hilbert space component* of Ψ. The functions ψ_p are not quadratically integrable. The operator $\mathcal{A}$ antisymmetrizes $\Theta_p\psi_p$ and is assumed here to include the factor $(N+1)^{-1/2}$ required to give this antisymmetrized function the same relative normalization as an $N+1$-electron Slater determinant.

The wave function Ψ can be taken to be an eigenfunction of $\mathbf{L}^2$, $\mathbf{S}^2$, and of parity. The Hilbert space component function Ψ_H can be expanded in antisymmetrized LS-eigenfunctions. Since these in turn can be expressed as linear combinations of Slater determinants, the expansion indicated in Eq. (1) is completely general. The *a priori* construction of LS-eigenfunctions can be considered as a matter of computational convenience. In the first implementation of the present method, LS-eigenfunctions have *not* been constructed explicitly. The method will be described here in terms of simple Slater determinants as a basis for the $N+1$-electron Hilbert space. The wave function Ψ has well defined values of M_L, M_S, and parity, but in general will be a superposition of noninteracting LS-components.

The Slater determinants Φ_μ are defined in terms of virtual excitations of an N-electron reference determinant Φ_0, itself defined as an antisymmetrized product of N orthonormal *occupied* orbital functions $\phi_i, \phi_j, \ldots$. Virtual excitations are defined by replacing some n specified occupied orbitals of Φ_0 by $n+1$ one-electron functions drawn from a set of *unoccupied* orbitals $\phi_a, \phi_b, \ldots$ that are mutually orthonormal but orthogonal to the occupied set. The orbitals are quadratically integrable functions of space and spin variables. An assumed countable complete set of normalizable orbitals $\{\phi_i; \phi_a\}$ generates a uniquely defined basis $\{\Phi_\mu\}$ for the $N+1$-electron Hilbert space. A typical Slater determinant Φ_μ can be denoted by

$$\Phi_{ij\ldots}^{abc\ldots}, \qquad i<j<\cdots\leqslant N<a<b<c<\cdots, \tag{3}$$

where the notation implies that $(\phi_a, \phi_b, \phi_c, \ldots)$ replace $(\phi_i, \phi_j, \ldots)$ in reference to the determinant Φ_0, in the order specified. Appropriate normalization of Φ_μ is implied. As examples of this notation,

$$\begin{aligned} \Phi^a &= \det \phi_1(1) \cdots \phi_i(i) \cdots \phi_N(N)\, \phi_a(N+1), \\ \Phi_i^{ab} &= \det \phi_1(1) \cdots \phi_a(i) \cdots \phi_N(N)\, \phi_b(N+1), \ldots \end{aligned} \tag{4}$$

A general computational procedure of successive variational calculations, using nested subspaces of the Hilbert space $\{\Phi_\mu\}$, has been discussed in detail elsewhere [2, 5]. This computational procedure for the scattering problem, used in the present work, is equivalent to variational solution of a hierarchy of continuum Bethe–Goldstone equations.

An oscillatory function of nonvanishing asymptotic amplitude cannot be represented as a finite superposition of quadratically integrable orbitals. For this reason, the part of Ψ indicated in Eq. (1) that contains the open-channel orbitals ψ_p remains distinct from the Hilbert space component for any calculation using a finite set of orbitals from the countable complete set $\{\phi_i;\ \phi_a\}$. Each open-channel orbital function is of the form

$$\psi_p = f_p(r)\, Y_{lm_l}(\theta, \phi)\, v_{m_s}, \tag{5}$$

where the quantum numbers l, m_l, m_s are determined by the channel index p. The radial function $f_p(r)$ satisfies the usual bound–state boundary conditions at $r = 0$ and is orthogonal (by construction) to all radial functions for normalizable orbitals with the same angular and spin quantum numbers. For scattering by a neutral atom in a unique, nondegenerate state the asymptotic form of f_p is

$$f_p(r) \sim k_p^{-1/2} r^{-1} \sin(k_p r - \tfrac{1}{2} l_p \pi + \delta_p). \tag{6}$$

This functional form must be suitably modified for scattering by a Coulomb or dipole potential. For multichannel scattering f_p can be written in the form

$$f_p = \sum_{i=0,1} F_{ip} \alpha_{ip}, \tag{7}$$

where

$$\begin{aligned} F_{0p} &= S_p \sim k_p^{-1/2} r^{-1} \sin(k_p r - \tfrac{1}{2} l_p \pi), \\ F_{1p} &= C_p \sim k_p^{-1/2} r^{-1} \cos(k_p r - \tfrac{1}{2} l_p \pi). \end{aligned} \tag{8}$$

These functions are constructed to satisfy the same boundary condition at $r = 0$ and the same orthogonality conditions as f_p. This ensures that the open-channel part of Ψ, given by the first term in Eq. (1), is orthogonal to the Hilbert space $\{\Phi_\mu\}$.

A target atom wave function Θ_p can be expressed in the form

$$\Theta_p = \sum_\sigma \Phi_\sigma c_\sigma{}^p, \tag{9}$$

where each Φ_σ is a normalized N-electron determinant constructed from the orbital functions $\{\phi_i;\ \phi_a\}$. The coefficients $c_\sigma{}^p$ are obtained as a normalized eigenvector of the N-electron Hamiltonian matrix $H_{\sigma\sigma'}$, corresponding to energy eigenvalue E_p. If E is the total energy of the system, an open-channel k value is defined by

$$\tfrac{1}{2} k_p{}^2 = E - E_p \tag{10}$$

if $E - E_p$ is nonnegative. Energies here are in Hartree atomic units.

In consequence of linearity, Eq. (1) can be expressed in the form

$$\Psi = \sum_i \sum_p \Big(\Theta_{ip} + \sum_\mu \Phi_\mu c_\mu^{ip}\Big)\, \alpha_{ip}, \tag{11}$$

with

$$\Theta_{ip} = \sum_{\sigma} \Phi_{\sigma}^{ip} c_{\sigma}{}^{p}, \tag{12}$$

where the coefficients $c_{\sigma}{}^{p}$ are the target state eigenvector coefficients of Eq. (9), and the coefficients α_{ip}, with $i = 0, 1$, are defined in Eq. (7). The functions Φ_{σ}^{ip} are unnormalized (not quadratically integrable) $N + 1$-electron Slater determinants

$$\Phi_{\sigma}^{ip} = \mathscr{A}\Phi_{\sigma} F_{ip} \tag{13}$$

defined in terms of the functions S_p, C_p of Eqs. (8).

The coefficients c_{μ}^{ip}, Eq. (11), can be obtained separately for each set of indices i, p from the matrix equations

$$\Big(\Phi_{\mu} \mid H - E \mid \Theta_{jq} + \sum_{\nu} \Phi_{\nu} c_{\nu}^{jq}\Big) = 0, \qquad \text{all } \mu, j, q. \tag{14}$$

Here H is the $N + 1$-electron Hamiltonian operator. These equations follow from the variational condition

$$\partial \Xi / \partial c_{\mu}^{ip*} = 0, \qquad \text{all } \mu, i, p, \qquad \text{all } \alpha_{jq}, \tag{15}$$

where the variational functional is

$$\Xi = (\Psi \mid H - E \mid \Psi). \tag{16}$$

When Eqs. (14) are satisfied, the variational functional becomes an explicit quadratic function of the coefficients α_{ip}:

$$\Xi = \sum_{ip} \sum_{jq} \alpha_{ip}^{*} m_{ij}^{pq} \alpha_{jq}, \tag{17}$$

where, in consequence of Eqs. (14),

$$m_{ij}^{pq} = M_{ij}^{pq} - \sum_{\mu} \sum_{\nu} M_{ip,\mu} (M^{-1})_{\mu\nu} M_{\nu,jq}. \tag{18}$$

The principal computational effort in the present method is calculation of the matrix m_{ij}^{pq}.

The matrices combined in Eq. (18) are the *bound–bound matrix* (Hermitian)

$$M_{\mu\nu} = (\Phi_{\mu} \mid H - E \mid \Phi_{\nu}); \tag{19}$$

the *bound–free matrix*

$$M_{\mu,ip} = (\Phi_{\mu} \mid H - E \mid \Theta_{ip}); \tag{20}$$

and the *free-free matrix* (non-Hermitian)

$$M_{ij}^{pq} = (\Theta_{ip} \mid H - E \mid \Theta_{jq}). \tag{21}$$

The matrix elements in Eq. (18) can be written as

$$m_{ij}^{pq} = \Big(\Theta_{ip} \mid H - E \mid \Theta_{jq} + \sum_{\nu} \Phi_\nu c_\nu^{jq}\Big). \tag{22}$$

Then if Ψ is an exact solution of the Schrödinger equation,

$$(H - E)\Psi = 0,$$

the coefficients α must satisfy the matrix equations

$$\sum_{jq} m_{ij}^{pq} \alpha_{jq} = 0, \qquad \text{all } i, p. \tag{23}$$

For N_C open channels, these equations have N_C linearly independent solutions. Since the asymptotic wave function is specified through Eqs. (7) and (8) entirely by the coefficients α, these coefficients determine physical scattering cross sections.

It is convenient to use a matrix notation in which channel indices p, q are suppressed, but matrices and vectors are segmented according to the indices $i, j = 0, 1$. In this notation the matrix generalization of Eq. (17) is

$$\begin{aligned} \Xi &= \alpha^\dagger m \alpha \\ &= \alpha_0{}^\dagger(m_{00}\alpha_0 + m_{01}\alpha_1) + \alpha_1{}^\dagger(m_{10}\alpha_0 + m_{11}\alpha_1), \end{aligned} \tag{24}$$

and Eqs. (23), for an exact scattering solution, are

$$m\alpha = \begin{pmatrix} m_{00} & m_{01} \\ m_{10} & m_{11} \end{pmatrix} \begin{pmatrix} \alpha_0 \\ \alpha_1 \end{pmatrix} = 0. \tag{25}$$

Here α denotes the $2N_C \times N_C$ rectangular matrix consisting of N_C linearly independent column vector solutions of Eqs. (25). The symbol (†) denotes an Hermitian adjoint, or transpose of a real matrix.

The reactance matrix K is defined by a matrix solution of Eqs. (25) in the form

$$\begin{aligned} \alpha_0 &= I, \\ \alpha_1 &= K, \end{aligned} \tag{26}$$

where I is the $N_C \times N_C$ unit matrix. An arbitrary solution matrix α can be reduced to this form by multiplying on the right by α_0^{-1}, assuming that α_0 is not singular. Then in general

$$K = \alpha_1 \alpha_0^{-1}.$$

Alternatively,

$$K^{-1} = \alpha_0 \alpha_1^{-1}. \tag{27}$$

For exact scattering solutions, the reactance matrix is real and symmetric [9]. Scattering and transition matrices are defined, respectively, by

$$S = (I + iK)(I - iK)^{-1}, \tag{28}$$

$$T = -2K(I - iK)^{-1}. \tag{29}$$

The partial cross section for scattering from channel p to channel q is, in atomic units,

$$\begin{aligned} Q_{pq} &= (\pi/k_p^2)|\, T_{pq}\,|^2 \\ &= (4\pi/k_p^2)|[K(I - iK)^{-1}]_{pq}\,|^2. \end{aligned} \tag{30}$$

The free–free matrix of Eq. (21) is not symmetric. The kinetic-energy operator in H, when acting on open-channel orbitals with asymptotic form specified by Eqs. (8), gives rise to a surface integral such that

$$M_{ij}^{pq} - M_{ji}^{qp} = \tfrac{1}{2}\delta_{pq}(\delta_{i0}\delta_{j1} - \delta_{i1}\delta_{j0}). \tag{31}$$

The same formula holds for m_{ij}^{pq}. In matrix notation this is

$$m_{01} - m_{10}^{\dagger} = \tfrac{1}{2}I. \tag{32}$$

Eq. (25) is a system of $2N_C$ homogeneous equations for $2N_C$ unknown coefficients, where N_C linearly independent solutions are sought. This requires that the unsymmetric matrix m have N_C distinct zero eigenvalues. In general this occurs only in the limit of an exact solution of the scattering equations. Variational methods, based on those originally proposed by Kohn and Hulthén [10], are used to obtain coefficients α appropriate to a given matrix m_{ij}^{pq}. Among several alternative methods, model calculations indicate that the OAF (optimized anomaly-free) method, to be described here, is generally the most accurate [2].

In the OAF method, the $2N_C$-dimensional linear space of the asymptotic partial wave functions is transformed by a unitary matrix

$$u = (\alpha \quad \beta), \tag{33}$$

where α and β are both $2N_C \times N_C$ matrices, each representing N_C orthonormal column vectors. The transformed matrix m is

$$m' = u^{\dagger} m u \tag{34}$$

$$= \begin{pmatrix} m'_{00} & m'_{01} \\ m'_{10} & m'_{11} \end{pmatrix} = \begin{pmatrix} \alpha^{\dagger} m \alpha & \alpha^{\dagger} m \beta \\ \beta^{\dagger} m \alpha & \beta^{\dagger} m \beta \end{pmatrix}. \tag{35}$$

The transformation is determined by the condition that m' should be in upper-triangular form, so that

$$m'_{10} = \beta^{\dagger} m \alpha = 0, \tag{36}$$

with all diagonal elements of m'_{00} less in magnitude than those of m'_{11}. Since the variational functional is

$$\Xi = \alpha^{\dagger} m \alpha = m'_{00}, \tag{37}$$

this minimizes the determinant of Ξ.

The variational coefficient matrix $[\alpha]$ is expressed in terms of this preliminary transformation by [2]

$$[\alpha] = \begin{pmatrix} \alpha_0 + \beta_0 [K'] \\ \alpha_1 + \beta_1 [K'] \end{pmatrix}, \tag{38}$$

where

$$[K'] = -(m'_{01})^{-1} m'_{00}. \tag{39}$$

It can be shown that $[K']$ is stationary with respect to variations about a zero trial matrix [2]. The reactance matrix $\alpha_1 \alpha_0^{-1}$ is

$$K = (\alpha_1 + \beta_1 [K'])(\alpha_0 + \beta_0 [K'])^{-1}. \tag{40}$$

3. COMPUTATIONAL ALGORITHMS

This section gives details of the algorithms used in each stage of computation. A master diagram is shown in Fig. 1.

The initial stages of an electron–atom scattering calculation make use of algorithms and programs described some time ago [11] that are also used for bound–state calculations. A matrix Hartree–Fock calculation is carried out for a reference target atom Slater determinant Φ_0, whose occupied orbitals are specified in terms of their quantum numbers (n, l, m_s, m_l). Radial basis orbitals, of the form

$$r^{\nu-1} \exp(-\zeta r), \tag{41}$$

are specified by a list of exponents ζ for each pair of indices $(\nu\, l)$ in a given range. Matrix elements appropriate to bound–state calculations are computed by the program ONECI [11] and used for a matrix Hartree–Fock calculation by the program SCF [11]. This calculation defines not only the occupied orbitals ϕ_i of Φ_0 but also a complementary set ϕ_a of orthonormal orbitals, obtained by diagonalizing the matrix of the Hartree–Fock effective Hamiltonian $\mathscr{H}_0$ over the full linear space

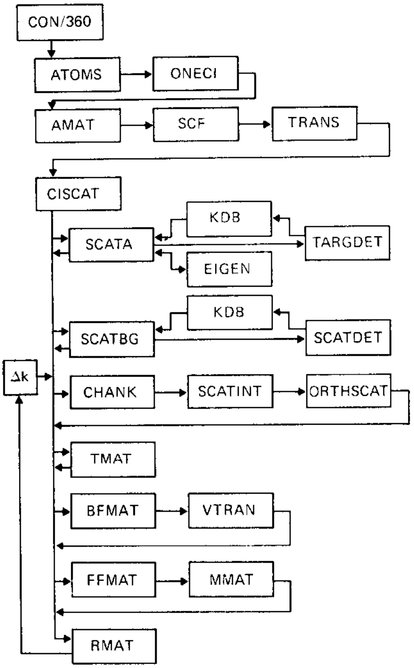

FIG. 1. Map of implementing programs.

spanned by all basis orbitals. The unoccupied orbitals ϕ_a are used in the definition of virtual excitations throughout the remaining stages of computation. They will be defined here by conventional quantum numbers ($n\ l$), but the "principal quantum number" n is used merely as a counting index for orbitals ordered by increasing values of $(\phi_a \mid \mathscr{H}_0 \mid \phi_a)$, and does not have the usual physical connotation. In particular the energies $(\phi_a \mid \mathscr{H}_0 \mid \phi_a)$ are almost always positive, and the orbitals ϕ_a must be thought of as arbitrarily defined wave packets in the continuum of the operator $\mathscr{H}_0$ [11].

The program TRANS [11] transforms the reduced matrix elements of the two-electron Coulomb potential into the representation with orthonormal basis $\{\phi_i;\ \phi_a\}$. The corresponding transformation of one-electron operators (kinetic energy and nuclear attraction) is carried out by SCF.

The transformed matrices, to be used as input data at later stages of the scattering calculation, are stored in a general scratch data filing system managed by the program CON/360. This program, which is used throughout the current implementation of the present method, has been described elsewhere [12]. It serves as a monitor and outer loop for all other programs, and also provides various data handling services through subroutine calls. CON/360 controls dynamical overlay, so that program segments (modules) can be loaded, entered, or deleted on request from the currently operating program.

The program CISCAT, indicated in Fig. 1, is the driving program for scattering calculations. The specific subprograms that it controls are described in the following Sections.

The initial program ATOMS and several others not indicated in Fig. 1, read or modify input data to be used by the bound-state programs.

A. *Construction of Target States* (SCATA, TARGDET)

States of the target atom are specified by supplying a list of configurations, defined in terms of virtual excitations of the reference configuration. A reference channel, for elastic scattering by the target reference state, is defined by specifying channel orbital parity and quantum numbers m_s, m_l. The target reference state quantum numbers are those of determinant Φ_0. A maximum angular quantum number $\bar{l}$ is also specified. This information suffices to determine the total ($N + 1$-electron) quantum numbers for Ψ, and to define allowed ranges of the (N-electron) quantum numbers for target atom states from the specified configurations.

The program SCATA indicated in Fig. 1, provides an outer loop for the construction of target atom states. It builds up a list of possible N-electron quantum numbers (π, M_S, M_L). For each entry in this list, the list of target atom configurations is expanded into a list of Slater determinants by program module TARGDET, which then calls KDB (described below) to construct the matrix of the N-electron Hamiltonian with this determinant list as basis. This matrix is then diagonalized by a standard Jacobi program EIGEN and the resulting eigenvalues and eigenvectors are added to a stored list for later use. This process is repeated until the list (π, M_S, M_L) is exhausted. Modules KDB and TARGDET are overlayed by EIGEN each time the latter is used.

For each target atom configuration in the input list, TARGDET constructs a list of all Slater determinants with given quantum numbers (π, M_S, M_L). While construction of LS-eigenfunctions could be done by an orthogonal transformation of this linear space, this is *not* done in the present programs. Nevertheless, because of the symmetry of the N-electron Hamiltonian, the eigenvectors eventually obtained by EIGEN are necessarily LS-eigenfunctions. Because the target configuration-interaction matrices are relatively small, and because this stage of computation bears very little weight in a scattering calculation, no significant computational advantage would be gained by explicit construction of symmetry-adapted target functions prior to the matrix diagonalization.

An encoded notation has been developed for the description of configurations, Slater determinants, and orbital wave functions. This notation makes it possible to list, index, or modify these symbolic entities by arithmetic or logical operations.

Each orbital function, including spin and angular factors, is specified by four indices: l, n, m_s, m_l. For occupied orbitals of the reference determinant, n has the usual meaning of the principal quantum number, but for unoccupied orbitals, n as used here is simply a counting index. These four indices define a single integer, denoted here by i or a, respectively, for occupied and unoccupied orbitals:

$$i \quad \text{or} \quad a = l\mu^3 + n\mu^2 + s\mu + m, \tag{42}$$

where μ is a convenient base integer, and

$$\begin{aligned} l &= 0, 1, \ldots, \\ n &= l + 1, l + 2, \ldots, \\ s &= m_s + \tfrac{1}{2}, \\ m &= m_l + \tfrac{1}{2}\mu. \end{aligned} \tag{43}$$

This index integer can be denoted by $(l\, n\, s\, m)$. It is uniquely defined if μ exceeds the maximum range of any of the subindices.

The notation for Slater determinants, indicated in Eqs. (4), defines an N-electron determinant $\Phi_{ij\ldots}^{ab\ldots}$ in terms of $\bar{n}$ virtual excitations a/i of the N-electron determinant Φ_0. This is encoded as a list of $2\bar{n} + 1$ integers:

$$\bar{n}, a_1, i_1, a_2, i_2, \ldots, a_{\bar{n}}, i_{\bar{n}}. \tag{44}$$

By convention, $a_1 < a_2 < \cdots$, and $i_1 < i_2 < \cdots$.

A *configuration* can be defined as the linear space spanned by all Slater determinants with common values of the orbital subindices $(l\, n)$. The basis for a configuration is the set of Slater determinants with given $(l\, n)$ values, for all possible selections of m_s and m_l. This basis can be further subdivided according to values of

$$M_S = \textstyle\sum m_s, \qquad M_L = \sum m_l. \tag{45}$$

A virtual excitation notation is used for configurations. This is encoded as the list

$$\bar{N}, A_1, I_1, \ldots, A_{\bar{N}}, I_{\bar{N}}, \tag{46}$$

where $A_1 \leqslant A_2 \leqslant \cdots$, and $I_1 \leqslant I_2 \leqslant \cdots$. These integers are defined by

$$I \quad \text{or} \quad A = l\mu^3 + n\mu^2, \tag{47}$$

obtained from $(l\, n\, s\, m)$ by setting $s = m = 0$. If μ exceeds $2l + 1$, zero cannot occur as a specific value of m, defined by Eq. (43).

These notations give concrete form to the operations of program modules SCATA and TARGDET, described above. The specific operation of TARGDET is to construct a determinant list as a string of the sublists defined by Eq. (44), given π, M_S, M_L and an input list of configurations. The total quantum numbers are specified indirectly in terms of integers $(\pi\, 0\, s\, m)_0$ and $(\pi\, 0\, s\, m)_P$, where

$$(\pi\, 0\, s\, m) = \pi\mu^3 + s\mu + m. \tag{48}$$

Here π is 0 or 1, to indicate orbital parity. The integer $(\pi\, 0\, s\, m)_0$ defines the reference channel orbital quantum numbers, and $(\pi\, 0\, s\, m)_P$ defines possible quantum numbers of a set of open-channel orbitals. The criterion used in accepting a determinant Φ_σ into the target state list for channel set P is

$$\Delta(\pi\, 0\, M_S\, M_L) = (\pi\, 0\, s\, m)_0 - (\pi\, 0\, s\, m)_P, \tag{49}$$

where

$$\Delta(\pi\, 0\, M_S\, M_L) = \sum_{k=1}^{\bar{n}} (a_k - i_k), \tag{50}$$

with the conventions that in $(l\, n\, s\, m)$, for each orbital, n is ignored and the sum over l is taken modulo 2. The sum in Eq. (50) is easily obtained by scanning the integer list used to define Φ_σ.

For an open-shell configuration, the list of Slater determinants for given configuration and total quantum numbers contains virtual excitation numbers

$$\bar{n} = \bar{N}, \bar{N} + 1, \ldots. \tag{51}$$

Here $\bar{n}$ can exceed $\bar{N}$ for the configuration because unoccupied orbitals can replace occupied orbitals of the same $(l\, n)$ subshell when the subshell is partially occupied. The algorithm for constructing the determinant list makes use of structured lists of occupied and unoccupied orbitals, $(l\, n\, s\, m)_i$ and $(l\, n\, s\, m)_a$, respectively, together with pointers to subshells and cross-linkage of each partially occupied subshell. The code for each configuration [Eq. (46)] is scanned to construct a list of indices d_i, d_a, giving the number of identical words I, A, respectively, in the configuration code, for each $(l\, n)$ subshell. By convention the configuration code has all entries I different from all entries A, since an identical replacement $(l\, n/l\, n)$ would be redundant in specifying a configuration. The list $\{d_i; d_a\}$ defines a *skeleton*, of order $\bar{n} = \bar{N}$, which is then filled in with $(s\, m)$ indices to give a list of Slater determinants, selected for the given values of (π, M_S, M_L). When partially occupied subshells occur, a sequence of skeletons, of increasing $\bar{n}$, are defined by considering identical replacements. Thus $d_i(l\, n)$ and $d_a(l\, n)$ are increased together for each partially occupied subshell $(l\, n)$, until either d_i or d_a has its maximum value, exhausting the available orbital set. All possible combinations of identical replacements for all partially occupied subshells are generated, each defining a skeleton with $\bar{n} \geqslant \bar{N}$, which in turn is used to generate a sublist of Slater determinants with given (π, M_S, M_L). This algorithm produces a complete, ordered list of determinants for any given configuration.

B. *Configuration–Interaction Matrix* (KDB)

The program module KDB constructs the configuration–interaction matrix (matrix of the N-electron Hamiltonian), given a basis list of Slater determinants. Module KDB is used in identical form in bound–state and scattering calculations, and has been used for extensive calculations of atomic energy levels and hyperfine structure [13]. It will be described briefly here because a published description is not available elsewhere.

If the N-electron Hamiltonian is written in the generalized form

$$H = \sum_{i} K(i) + \sum_{ij} Q(ij), \tag{52}$$

where $i = 1, \ldots, r$ and $i < j \leqslant N$, matrix elements of H between a given Slater determinant Φ_0 and any other determinant $\Phi_{ij\ldots}^{ab\cdots}$ can be expressed simply in terms of operators R and $\mathscr{H}_0$ defined by

$$(ab \mid R \mid cd) = (ab \mid Q \mid cd) - (ab \mid Q \mid dc) \tag{53}$$

and

$$\mathscr{H}_0 = K + \sum_{i(\mathrm{occ})} (i \mid R \mid i). \tag{54}$$

The matrix elements of H are [14, 15]

$$\begin{aligned} (\Phi_{ijk\ldots}^{abc\cdots} \mid H \mid \Phi_0) &= 0, && \text{more than 2 substitutions;} \\ (\Phi_{ij}^{ab} \mid H \mid \Phi_0) &= (ab \mid R \mid ij), && \text{2 substitutions;} \\ (\Phi_i{}^a \mid H \mid \Phi_0) &= (a \mid \mathscr{H}_0 \mid i), && \text{1 substitution.} \end{aligned} \tag{55}$$

Diagonal elements are given by [15]

$$\begin{aligned} &(\Phi_{ij\ldots}^{ab\cdots} \mid H \mid \Phi_{ij\ldots}^{ab\cdots}) - \Phi_0 \mid H \mid \Phi_0) \\ &\quad = (a \mid \mathscr{H}_0 \mid a) + (b \mid \mathscr{H}_0 \mid b) + \cdots - (i \mid \mathscr{H}_0 \mid i) - (j \mid \mathscr{H}_0 \mid j) - \cdots \\ &\qquad + (ab \mid R \mid ab) + \cdots + (ij \mid R \mid ij) + \cdots - (ai \mid R \mid ai) - \cdots. \end{aligned} \tag{56}$$

These formulas depend only on the specific indices contained in the substitution notation used here.

For general matrix elements $(\Phi_\mu \mid H \mid \Phi_\nu)$, with Slater determinants Φ_μ and Φ_ν both defined by virtual excitation (substitution notation) from a reference determinant Φ_0, it is necessary to express Φ_μ as a virtual excitation of Φ_ν before applying Eqs. (55), with $\mathscr{H}_0$ replaced by

$$\mathscr{H}_\nu = \mathscr{H}_0 + \sum_{a(\nu)} (a \mid R \mid a) - \sum_{i(\nu)} (i \mid R \mid i). \tag{57}$$

Here $a(\nu)$ and $i(\nu)$ are the virtual excitation indices of Φ_ν in the notation $\Phi_{ij\ldots}^{ab\cdots}$. These formulas are used explicitly by module KDB to construct the matrix $H_{\mu\nu} - H_{00}\delta_{\mu\nu}$.

The matrix element $(\Phi_\mu \mid H \mid \Phi_\nu)$ is reduced by a simple algorithm that uses the substitution notation directly. Given

$$\Phi_\mu\colon m, a_{1\mu}, i_{1\mu}, \ldots, a_m, i_m; \tag{58}$$

$$\Phi_\nu\colon n, a_{1\nu}, i_{1\nu}, \ldots, a_n, i_n, \tag{59}$$

this algorithm produces a similar list defining Φ_μ as a virtual excitation of Φ_ν. A phase factor $(-1)^p$ is defined by the number of orbital interchanges required to match as many as possible occupied orbitals of Φ_μ to those of Φ_ν.

The code for Φ_ν is scanned and each element i_ν is compared with all elements i_μ of the Φ_μ code. If a match is found, the element i_μ is replaced by a_ν corresponding to the matched element i_ν. If i_ν differs from all i_μ the pair of elements i_ν, a_ν are added in the stated order to the end of the Φ_μ list, and m is increased by one.

When the Φ_ν code is exhausted, the resulting modified Φ_μ list is scanned, and each element $i_{j\mu}$ (in the extended list) is compared with every element $a_{b\mu}$. If a match is found, element $a_{j\mu}$ is replaced by $a_{b\mu}$, elements in positions $i_{j\mu}$ and $a_{j\mu}$ are deleted (set to zero), the sign of $(-1)^p$ is reversed ($p = 0$ initially), and m is decreased by one.

It can easily be verified that the final modified Φ_μ list (ignoring zeroes) is the virtual excitation code for Φ_μ relative to Φ_ν, that the degree of excitation is given by the final value of m, and that the phase factor for matrix elements is the final value of $(-1)^p$.

Matrix elements $(ab \mid R \mid cd)$ required by KDB are defined by Eq. (53) in terms of matrix elements of Q. Angular integration gives the formula [14]

$$(ab \mid Q \mid cd) = \sum_\lambda c^\lambda(a; c)\, c^\lambda(d; b)[ac \mid db]^\lambda, \tag{60}$$

where $c^\lambda(a; c)$ is a Gaunt coefficient [16, 14] and $[ac \mid db]^\lambda$ is a reduced matrix element of the electronic Coulomb potential (generalized Slater parameter)

$$[ac \mid db]^\lambda = \int_0^\infty dr_1 \int_0^\infty dr_2\, (r_<^{\lambda+2}/r_>^{\lambda-1})\, R_a{}^*(r_1)\, R_c(r_1)\, R_d(r_2)\, R_b{}^*(r_2). \tag{61}$$

Tables of these reduced matrix elements are produced by module TRANS in a format, described earlier [11], that facilitates table look-up. Tables of Gaunt coefficients are also produced at an earlier stage of calculation, and used by KDB through a simple table look-up algorithm.

Matrix elements of $\mathscr{H}_0$ are tabulated by program module SCF [11] in the case of a closed-shell reference state. In the more general case, matrix elements of an averaged operator

$$\mathscr{H}_{Av} = [\mathscr{H}_0]_l , \tag{62}$$

as defined previously [11], are tabulated by SCF. Matrix elements of $\mathscr{H}_0$ required by KDB are obtained from these tabulated elements by adding linear combinations of matrix elements $(ab \mid Q \mid cd)$, with coefficients that depend explicitly on m_l quantum numbers through the Gaunt coefficients of Eq. (60), and also on m_s quantum numbers. These coefficients, required only for incomplete shells of the reference determinant Φ_0, are tabulated with input data required by program module AMAT, which constructs matrices used by SCF.

C. *Construction of Bound Component* (SCATBG, SCATDET)

The bound or Hilbert space component Ψ_H of the $N + 1$-electron wave function, indicated in Eq. (2), is expanded as a linear combination of $N + 1$-electron Slater determinants. At a given level of the hierarchy of variational Bethe–Goldstone equations used in the present work [2, 5], the basis for Ψ_H is the set of Slater determinants obtained by all possible virtual excitations of occupied orbitals $\{\phi_i\}$ forming a specified subset of the occupied orbitals of the reference state. These virtual excitations are of the kind indicated in Eqs. (4), with $n + 1$ unoccupied orbitals $a, b, \ldots$ replacing n occupied orbitals $\phi_i, \ldots$. These virtual excitations are defined in terms of configurations, as in previous bound–state calculations [17], so that a given level of the hierarchy of variational calculations is specified by a list of occupied subshell quantum numbers $(l\, n)$, with the allowed excitation level of each. In analogy to Eqs. (44) and (46) this is encoded as the list

$$m, I_1, I_2, \ldots, I_n , \tag{63}$$

where $m \leqslant n$ and $I_1 \leqslant I_2 \leqslant \cdots$. The integers I are defined as in Eq. (46), each denoting an occupied subshell of the reference determinant Φ_0. This notation defines the basis for Ψ_H as all virtual excitations of the configuration of Φ_0 indexed by any subset of up to m of the subshell indices $I_1, \ldots, I_n$, which may be repeated up to the original occupancy number in Φ_0.

The program SCATBG loads KDB and serves as a calling program for SCATDET, which reads the Bethe–Goldstone code data of Eq. (63), and then constructs the list of $N + 1$-electron Slater determinants defined by this code. The code is used to generate the implied sequence of configurations, each of which is expanded to a list of determinants using the same algorithm as TARGDET. In the present case, total quantum numbers (π, M_S, M_L) are those of the full wave function Ψ, so the acceptance criterion replaces Eq. (49) by

$$\Delta(\pi\, 0\, M_S\, M_L) = (\pi\, 0\, s\, m)_0 . \tag{64}$$

Since the number of unoccupied orbital indices a exceeds the number of occupied indices i, an $N + 1$-electron Slater determinant is encoded as a list of $2\bar{n} + 1$ integers

$$\bar{n}, a_1, i_1, \ldots, a_{\bar{n}}, -1, \tag{65}$$

where $a_1 < a_2 < \cdots$, $i_1 < i_2 < \cdots$, and the number of unoccupied orbitals is $\bar{n} \geqslant 1$.

When this determinant list is completed, SCATDET is deleted, and program module KDB is used to construct the $N + 1$-electron *bound-bound* matrix $H_{\mu\nu}$ for determinants Φ_μ, Φ_ν in the Hilbert space basis. The algorithm described above for KDB works correctly for the modified determinant codes indicated in Eq. (65), so KDB is used without modification. It produces the real symmetric bound-bound matrix, stored in lower triangular form for subsequent use. This matrix may be very large, and must be stored on auxiliary memory devices (disk and tape units in the present implementation).

When the target atom configuration list used by TARGDET contains more than the configuration of Φ_0, combination with an arbitrary additional bound orbital implies a set of $N + 1$-electron configurations. This set is always included by SCATDET even if not explicitly required by the Bethe–Goldstone code.

D. *Selection of Open Channels* (CHANK)

Program module CHANK is entered from CISCAT with the current reference channel k value. This determines total energy

$$E = E_0 + \tfrac{1}{2}k^2, \tag{66}$$

where E_0 is the lowest target energy eigenvalue obtained for the set of configurations containing the reference configuration. CHANK examines all target atom eigenstates obtained by SCATA and determines open channels p such that for a target energy eigenvalue E_p,

$$\tfrac{1}{2}k_p^2 = E - E_p \geqslant 0. \tag{67}$$

When this criterion is satisfied, the eigenvector and basis N-electron determinant list corresponding to E_p are abstracted from master lists stored by SCATA, and are placed in open-channel lists in order of decreasing k_p. This information completely defines the wave functions Θ_p of Eq. (9). Open-channel orbital quantum numbers $(l\, n\, s\, m)_p$ are also abstracted from data stored by SCATA. A condensed list of distinct k_p values is constructed by CHANK. These parameters define the external orbital functions F_{ip} of Eqs. (8).

E. *Channel Orbital Integrals* (SCATINT)

In the present implementation of the variational method, asymptotic oscillatory (free) functions are explicitly represented by spherical Bessel functions. Matrix elements of the electronic Hamiltonian operator are linear combinations of reduced matrix elements of the one-electron kinetic and nuclear potential energy operators, and of the two-electron Coulomb potential. Normalizable (bound) basis functions are chosen to be of the general form

$$r^{n-1}\exp(-\zeta r)\, Y_{lm}(\theta, \phi). \tag{68}$$

Reduced matrix elements for bound orbitals only are given by simple recurrence formulas, published some time ago [11]. Reduced matrix elements involving one or two free functions are computed by methods given in detail elsewhere [18]. These details will not be repeated here.

Since very large numbers of many-electron matrix elements are constructed from relatively smaller lists of basic integrals (reduced matrix elements), these integrals are tabulated when first computed by program module SCATINT, then read from the tables as required. The structure of these tables and the table look-up algorithms will be described here. These tables are stored by the general scratch data storage system used in the present work (CON/360), and then retrieved in whole or in part on demand.

A simplified notation will be used here for functions, operators, and matrix [redacted] Gaunt coefficients, as indicated in Eq. (60) for two-electron integrals. Tabulated reduced matrix elements depend only on the bound and free radial functions, which will be denoted here by lower-case indices $\{a\}$ for bound functions and by capital indices $\{A\}$ for free functions. Specifically, a^0 denotes the radial basis function, with angular quantum number l_a and normalization constant N_a,

$$R_a{}^0(r) = N_a r^{n_a-1}\exp(-\zeta_a r). \tag{69}$$

The free basis functions denoted by $A_i{}^0$ are, for $i = 0, 1$,

$$\begin{aligned} R^0_{0A}(r) &= k_A j_{l_A}(k_A r), \\ R^0_{1A}(r) &= -k_A\left[j_{l_A+1}(k_A r) + \frac{l_A+1}{k_A r}\, j_{l_A+2}(k_A r)\right]. \end{aligned} \tag{70}$$

When divided by $k_A^{1/2}$ these functions have the asymptotic radial dependence required by Eqs. (8).

Two-electron reduced matrix elements are all of the form defined by Eq. (61). One-electron matrix elements are required for the operators, in Hartree units,

$$T = -\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{2r^2}, \tag{71}$$

and

$$K = T - \frac{Z}{r}, \tag{72}$$

where Z is the nuclear charge. The auxiliary radial operator $\mathscr{H}_{Av}$ is defined by Eqs. (54) and (62) in terms of the shell structure of the reference state.

Computation, tabulation, and table look-up algorithms for integrals with all bound–state basis functions have been described elsewhere [11]. The new integrals required for variational scattering calculations are of the following types:

$$\begin{aligned} M_{11} &: (A_i^0 \mid T - \epsilon_B \mid B_j^0), \\ M_{12} &: (a^0 \mid K - \epsilon_B \mid B_i^0), \\ M_{13} &: (a^0 \mid B_i^0), \\ M_{21} &: [a^0 b^0 \mid C_i^0 D_j^0]^\lambda, \\ M_{22} &: [a^0 B_i^0 \mid c^0 D_j^0]^\lambda \\ M_{23} &: [a^0 b^0 \mid c^0 D_i^0]^\lambda, \end{aligned} \tag{73}$$

where ϵ_B is $k_B{}^2/2$. These basic integrals are computed directly [18].

All of these integrals can be stored and retrieved by making use of segmented tables, with simple formulas for the displacement of each integral within its segment. The full table is broken into five major segments, corresponding to M_{11}, M_{12} and M_{13} together, M_{21}, M_{22}, and M_{23}. A separate index table contains, in order, the five displacement addresses α_{11}, α_{12}, α_{21}, α_{22}, α_{23} and the major segment lengths $\Delta\alpha_{11}$, $\Delta\alpha_{12}$, $\Delta\alpha_{21}$, $\Delta\alpha_{22}$, $\Delta\alpha_{23}$. Units are those of the number representation of the integrals, and displacement addresses are relative to the origin of the integral table. This information makes it possible to load, edit, or relocate the individual major segments. It is followed in the index table by five displacement pointers n_{11}, n_{12}, n_{21}, n_{22}, n_{23} that locate minor segment indices with respect to the origin of the index table.

Each major segment of the integral table is broken into minor segments, each consisting of integrals with given orbital angular quantum numbers, l_a or l_A for bound or free orbitals, respectively. For each minor segment, there is a list of four integers in the index table, of the general form

$$\gamma, d_\gamma, \beta, \Delta\beta. \tag{74}$$

Here β is the displacement address of the minor segment relative to the origin of the relevant major segment, and $\Delta\beta$ is the minor segment length.

For one-electron integrals γ defines a minor segment of the integral table. For M_{11}, γ is the orbital angular quantum number $l_A = l_B$ of a sublist of free orbitals, and $d_\gamma = d_A$ is the number of free basis orbitals with this quantum number. For M_{12} and M_{13}, which are interleaved in the table, γ is the quantum number $l_a = l_B$ for a sublist of bound orbitals, and $d_\gamma = d_a$ is the number of bound basis orbitals with this quantum number.

For two-electron integrals γ is an integer constructed from the four l-values that define a minor segment of the major segment blocks indicated in Eqs. (73):

$$\begin{aligned} \gamma_{21} &= l_a\mu^3 + l_b\mu^2 + l_C\mu + l_D\,; && l_a \geqslant l_b\,, \quad l_C \geqslant l_D\,, \\ \gamma_{22} &= l_a\mu^3 + l_B\mu^2 + l_c\mu + l_D\,; && (l_a\,, L_B) \geqslant (l_c\,, l_D), \\ \gamma_{23} &= l_a\mu^3 + l_b\mu^2 + l_c\mu + l_D\,; && l_a \geqslant l_b\,, \end{aligned} \tag{75}$$

where μ is a convenient base integer, as in Eq. (42). The integer $d_\gamma = n_\lambda$ is the number of allowed values of λ in each case.

This information makes it possible, by first reading the index table, to load and relocate the individual minor segments. For one-electron integrals, blocks M_{11} and $M_{12}(M_{13})$, the integers γ occur in counting order, with $d_\gamma = 0$ for any empty list, so the minor segment index list displacement is determined by n_{11} or n_{12} and quantum number l_A or l_a. For two-electron integrals, n_{21}, n_{22}, or n_{23} are used to define the first relative address of index codes to be scanned for the required value of the packed index γ_{21}, γ_{22}, or γ_{23}, respectively.

Individual integrals within minor segments of the integral table are stored in an order that corresponds to a simple table look-up formula. For M_{11} integrals the order can be symbolized by

$$(A_i{}^0 \mid T - \epsilon_B \mid B_j{}^0){:}\ \{ij\}; \qquad B = 0,\ \ d_A - 1; \qquad A = 0,\ \ d_A - 1, \tag{76}$$

where the notation implies an indexing sequence with each indicated index range nested within those written to its right. The symbol $\{ij\}$ denotes the order

$$\begin{matrix} (A_0B_0), & (A_0B_1), & (A_1B_0), & (A_1B_1) & \text{if } A \geqslant B, \\ (A_0B_0), & (A_1B_0), & (A_0B_1), & (A_1B_1) & \text{if } A < B. \end{matrix} \tag{77}$$

The displacement address of an M_{11} integral, relative to the origin of the M_{11} major segment, is

$$\beta_{11}(l_A) + 4(Ad_A + B) + 2I + J, \tag{78}$$

where

$$\begin{matrix} I = i, & J = j & \text{if } A \geqslant B, \\ I = j, & J = i & \text{if } A < B. \end{matrix} \tag{79}$$

M_{12}, M_{13} integrals are listed in the order

$$(a^0 \mid K - \epsilon_B \mid B_i{}^0), (a^0 \mid B_i{}^0){:}\ i = 0, 1; \quad B = 0,\ d_B - 1; \quad a = 0,\ d_a - 1. \tag{80}$$

Displacement relative to the M_{12} major segment origin is

$$\beta_{12}(l_a) + 4(ad_B + B) + 2i + \begin{Bmatrix} 1, & 13 \text{ integral} \\ 0, & 12 \text{ integral} \end{Bmatrix}. \tag{81}$$

M_{21} integrals are listed in the order

$$[a^0b^0 \mid C_i{}^0D_j{}^0]^\lambda : \{ij\}; \qquad \{\lambda\}; \qquad D = 0, \quad \begin{Bmatrix} d_D - 1 \\ C \end{Bmatrix}_{S2}, \qquad C = 0, \quad d_C - 1;$$
$$b = 0, \quad \begin{Bmatrix} d_b - 1 \\ a \end{Bmatrix}_{S1}; \qquad a = 0, \quad d_a - 1. \tag{82}$$

Here $\{ij\}$ has the same meaning as in Eq. (76), except that number pairs $[(l_C, C), (l_D, D)]$ replace (A, B). The symbol $\{\lambda\}$ denotes the range of λ. The other symbols in curly brackets are conditional limits. The upper value holds if the subscript condition is false, otherwise the lower value holds. Condition $S2$ is $l_C = l_D$. Condition $S1$ is $l_a = l_b$.

The displacement of an M_{21} integral relative to the M_{21} segment origin is

$$\beta_{21}(l_al_bl_Cl_D) + 4n_\lambda \left[\begin{Bmatrix} ad_b + b \\ \tfrac{1}{2}a(a+1) + b \end{Bmatrix}_{S1} \begin{Bmatrix} d_Cd_D \\ \tfrac{1}{2}d_C(d_C+1) \end{Bmatrix}_{S2} \right.$$
$$\left. + \begin{Bmatrix} Cd_D + D \\ \tfrac{1}{2}C(C+1) + D \end{Bmatrix}_{S2} \right] + f(\lambda; ij), \tag{83}$$

where

$$f(\lambda; ij) = 2(\lambda - \lambda_{\min}) + 2I + J, \tag{84}$$

with I and J defined as in Eq. (78), on replacing (A, B) by $[(l_C, C), (l_D, D)]$. Successive values of λ differ by two, so the first term in $f(\lambda; ij)$ is a multiple of four.

In using Eq. (83), orbital indices for equivalent integrals must be permuted so that when $S1$ is true, $a \geqslant b$, and when $S2$ is true, $C \geqslant D$. It is assumed here and below that orbital indices are permuted so that the angular quantum numbers satisfy the ordering conventions indicated in Eqs. (75).

M_{22} integrals are listed in the order

$$[a^0B_i{}^0 \mid c^0D_j{}^0]^\lambda : \{ij\}; \qquad \{\lambda\}; \qquad D = 0, \quad \begin{Bmatrix} d_D - 1 \\ B \end{Bmatrix}_{S12, a=c};$$
$$c = 0, \quad \begin{Bmatrix} d_c - 1 \\ a \end{Bmatrix}_{S12}; \qquad B = 0, \quad d_B - 1; \qquad a = 0, \quad d_a - 1. \tag{85}$$

Here the condition $S12$ is $(l_a, l_B) = (l_c, l_D)$. The symbol $\{ij\}$ refers to $[(l_B, B), (l_D, D)]$. The displacement of an M_{22} integral relative to the M_{22} segment origin is

$$\beta_{22}(l_al_Bl_cl_D) + 4n_\lambda \left[\begin{Bmatrix} (ad_B + \phi)\, d_cd_D \\ \tfrac{1}{2}(ad_B + B)(ad_B + B + 1) \end{Bmatrix}_{S12} + cd_D + D \right] + f(\lambda; ij), \tag{86}$$

where $f(\lambda; ij)$ is defined with reference to indices $[(l_B, B), (l_D, D)]$. When $S12$ is true, indices must be permuted so that $(a, B) \geqslant (c, D)$.

M_{23} integrals are listed in the order

$$[a^0b^0 \mid c^0D_i^0]^\lambda : i = 0, 1; \quad \{\lambda\}; \quad D = 0, \quad d_D - 1; \quad c = 0, \quad d_c - 1;$$
$$b = 0, \quad \begin{Bmatrix} d_b - 1 \\ a \end{Bmatrix}_{S1}; \quad a = 0, \quad d_a - 1. \tag{87}$$

The displacement of an M_{23} integral relative to the M_{23} major segment origin is

$$\beta_{23}(l_a l_b l_c l_D) + 2n_\lambda \left[\begin{Bmatrix} ad_b + b \\ \frac{1}{2}a(a + 1) + b \end{Bmatrix}_{S1} d_c d_D + cd_D + D \right] + g(\lambda; i), \tag{88}$$

where

$$g(\lambda; i) = (\lambda - \lambda_{\min}) + i. \tag{89}$$

When $S1$ is true, indices must be permuted so that $a \geqslant b$.

These formulas define compact, easily accessed tables that avoid redundancies by taking advantage of symmetries inherent in the definitions of the tabulated integrals. There are no structural restrictions on the range of angular quantum numbers.

F. *Orthogonalization* (ORTHSCAT)

The raw integrals computed by SCATINT are transformed in two ways before being used in the construction of many-electron matrix elements. These transformations are carried out by program module ORTHSCAT.

The one-electron operators T and K in integral blocks M_{11} and M_{12} are converted to the effective one-electron Hamiltonian $\mathscr{H}_{Av}$ of Eq. (62) by combining one- and two-electron integrals.

All integrals involving bound orbitals are transformed to an orthonormal basis of radial functions,

$$R_a = \sum_b x_{ab} R_b^0. \tag{90}$$

The transformation coefficients x_{ab} are computed by module SCF [11] and stored as square matrices. The free orbitals are orthogonalized to the Hilbert space of bound orbitals by the transformation

$$R_{iA} = R_{iA}^0 - \sum_a (A_i^0 \mid a)\, R_a\,. \tag{91}$$

M_{12} matrix elements are converted to $\mathscr{H}_{Av}$ by the formula [11]

$$(a^0 \mid \mathscr{H}_{Av} - \epsilon_B \mid B_i^0) = (a^0 \mid K - \epsilon_B \mid B_i^0) + \sum_\beta \sum_{(cd)_\beta} \rho^\beta(cd)\, A^\beta(cd \mid aB_i), \tag{92}$$

where

$$A^{\beta}(cd \mid aB_i) = \sum_{\lambda} C_D{}^{\lambda}[c^0d^0 \mid a^0B_i{}^0]^{\lambda} + \sum_{\lambda'} C_X^{\lambda'}([c^0a^0 \mid d^0B_i{}^0]^{\lambda'} + [d^0a^0 \mid c^0B_i{}^0]^{\lambda'}). \quad (93)$$

The coefficients $C_D{}^{\lambda}$ and $C_X^{\lambda'}$, sums of products of Gaunt coefficients, are available to ORTHSCAT as a table used in the program module AMAT, which constructs $A^{\beta}(cd \mid ab)$ for the target atom matrix Hartree–Fock calculation. The density matrix $\rho^{\beta}(cd)$ is computed and stored by program module SCF. In Eq. (92), β is used to index sets of occupied subshells of the target atom reference configuration that have the same structure [11]. The two-electron integrals in Eq. (93) are restricted to those for which $l_c = l_d$ and $l_a = l_B$. The allowed values of λ and λ' follow from the usual triangle rules for angular momentum quantum numbers.

Semitransformed M_{12} and M_{13} matrix elements are computed in the form

$$\begin{aligned} (a \mid \mathscr{H}_{Av} - \epsilon_B \mid B_i{}^0) &= \sum_c x_{ac}(c^0 \mid \mathscr{H}_{Av} - \epsilon_B \mid B_i{}^0) \\ (a \mid B_i{}^0) &= \sum_c x_{ac}(c^0 \mid B_i{}^0). \end{aligned} \quad (94)$$

These semitransformed matrices are stored for later use in the table format used for the raw M_{12}, M_{13} integrals, indicated in Eq. (80).

[redacted]

Matrix elements $(a \mid \mathscr{H}_{Av} \mid c)$ are computed and stored by program module SCF. The transformed integrals $(a \mid \mathscr{H}_{Av} - \epsilon_B \mid B_i)$ are stored together with $(a \mid B_i{}^0)$ in the table format defined by Eq. (80).

M_{11} matrix elements are converted to $\mathscr{H}_{Av}$ by the formula [11]

$$(A_i{}^0 \mid \mathscr{H}_{Av} - \epsilon_B \mid B_j{}^0) = (A_i{}^0 \mid T - \epsilon_B \mid B_j{}^0) + \sum_{\beta} \sum_{(cd)_{\beta}} \rho^{\beta}(cd)\, A^{\beta}(cd \mid A_iB_j), \quad (96)$$

where

$$A^{\beta}(cd \mid A_iB_j) = \sum_{\lambda \neq 0} C_D{}^{\lambda}[c^0d^0 \mid A_i{}^0B_j{}^0]^{\lambda} + \sum_{\lambda'} C_X^{\lambda'}([c^0A_i{}^0 \mid d^0B_j{}^0]^{\lambda'} + [d^0A_i{}^0 \mid c^0B_j{}^0]^{\lambda'}). \quad (97)$$

Notation here conforms to that of Eqs. (92) and (93). It has been shown previously that for a neutral target atom omission of the $\lambda = 0$ direct integrals $[cd \mid AB]$ in Eq. (97) exactly compensates for omission of the Coulomb potential $-Z/r$ from the M_{11} integrals $(A \mid T - \epsilon \mid B)$ [18]. The omitted integrals would diverge if integrated over $0 \leqslant r \leqslant \infty$.

The transformation of M_{11} integrals is completed by applying Eq. (91) to both A_i^0 and B_j^0 to produce integrals

$$\begin{aligned}(A_i \mid \mathscr{H}_{Av} - \epsilon_B \mid B_j) \\ &= (A_i^0 \mid \mathscr{H}_{Av} - \epsilon_B \mid B_j^0) - \sum_c (c \mid A_i^0)(c \mid \mathscr{H}_{Av} - \epsilon_B \mid B_j^0) \\ &\quad - \sum_c (c \mid \mathscr{H}_{Av} - \epsilon_A \mid A_i^0)(c \mid B_j^0) - \sum_c (\epsilon_A - \epsilon_B)(c \mid A_i^0)(c \mid B_j^0) \\ &\quad + \sum_c \sum_d (c \mid A_i^0)(c \mid \mathscr{H}_{Av} - \epsilon_B \mid d)(d \mid B_j^0). \qquad (98)\end{aligned}$$

These integrals are stored in the format defined by Eq. (76).

Transformation of the two-electron integrals to an orthogonal basis is straightforward, using first Eqs. (90) to refer all integrals to a basis of orthonormal bound orbitals, and then Eqs. (91). Semitransformed M_{23} integrals are stored and used in the final transformations of M_{21} and M_{22}. The two-electron integrals over four bound orthonormalized orbitals required for the final transformation are available in tables produced by program module TRANS [11]. Transformed integrals are stored in formats indicated by Eqs. (82), (85), and (87).

As an option, only a subset of the orthonormal radial functions $\{R_a\}$ may be used. Then x_{ab} in Eq. (90) is a rectangular matrix. The transformed integral tables produced by ORTHSCAT are accompanied by an index table revised from that produced by SCATINT in order to reflect these reductions of dimension and also the reordering of table segments necessitated by ORTHSCAT.

G. *Bound–Free and Free–Free Matrices* (BFMAT, FFMAT)

Elements of the bound–free matrix are defined by Eqs. (20) and (12),

$$M_{\mu,ip} = \sum_\sigma (\Phi_\mu \mid H - E \mid \Phi_\sigma^{ip})\, c_\sigma^{\,p}, \qquad (99)$$

where

$$\Phi_\sigma^{ip} = \mathscr{A}\Phi_\sigma F_{ip}\,. \qquad (100)$$

Since the open-channel orbital F_{ip} is orthogonalized to all bound orbitals, the matrix elements combined in Eq. (99) follow the rules for matrix elements between Slater determinants. Program module BFMAT uses the algorithm described above, with reference to module KDB, to construct bound–free matrix elements. Several necessary modifications will be described here.

The coefficients $\{c_\sigma\}$ for open channel p and the corresponding N-electron determinant list $\{\Phi_\sigma\}_p$ are computed by the target atom programs (SCATA, TARGDET, KDB), and stored in tables that are reread by BFMAT. A list of open-channel orbital codes $(l\,n\,s\,m)_p$, in the format defined by Eq. (42) for bound orbitals, is prepared by CHANK for use by BFMAT, together with index pointers to the corresponding segments of the coefficient and determinant lists, and a list of open-channel k_p values.

Since all of the matrix elements combined in Eq. (99) refer to the same pair of open-channel orbitals F_{ip} $(i = 0, 1)$, it is convenient to analyze these matrix elements in terms of the Slater determinants Φ_μ and Φ_σ. These are defined in substitution notation by integer list codes given by Eq. (65) for Φ_μ, an $N + 1$-electron determinant, and by Eq. (44) for Φ_σ, an N-electron determinant. The antisymmetrized function Φ_σ^{ip} could be encoded by appending $(l\,n\,s\,m)_p$, -1 to the code for Φ_σ. It can easily be verified that the matrix element algorithm of module KDB would give correct formulas for bound–free matrix elements if the Φ_σ code were extended in this way.

The same results are obtained, more simply, by applying the algorithm directly to the codes for Φ_μ and Φ_σ, except that the place of $(l\,n\,s\,m)_p$ is taken in the relative excitation code by "-1". The level of relative excitation Δn of Φ_μ with respect to Φ_σ, in this convention, is always at least one. Because of orbital orthogonality it follows, as in Eqs. (55), that the only nonvanishing matrix elements are of the form:

$$\Delta n = 1; \qquad \pm(c_1 \mid \mathscr{H}_\mu \mid F), \tag{101}$$

$$\Delta n = 2; \qquad \pm(c_1 c_2 \mid R \mid c_3 F), \tag{102}$$

where c_a denotes a bound orbital and F denotes F_{ip} $(i = 0, 1)$. Here the last of Eqs. (55) has been used in the equivalent form

$$(\Phi_i^a \mid H \mid \Phi_0) = (a \mid \mathscr{H}_0 \mid i) \equiv (a \mid \mathscr{H}_i^a \mid i), \tag{103}$$

where $\mathscr{H}_i^a$ is defined by Eq. (57).

In BFMAT, the further analysis of matrix elements given by Eqs. (101) and (102) follows the pattern of KDB in detail. For $\Delta n = 2$, $(c_1 c_2 \mid R \mid c_3 F)$ reduces to a sum of M_{23} integrals, multiplied by products of Gaunt coefficients, as indicated by Eqs. (53) and (60). For $\Delta n = 1$,

$$(c_1 \mid \mathscr{H}_\mu \mid F) = (c_1 \mid \mathscr{H}_0 \mid F) + \sum_{a(\mu)} (a c_1 \mid R \mid a F) - \sum_{i(\mu)} (i c_1 \mid R \mid i F). \tag{104}$$

The R-integrals reduce as in the case $\Delta n = 2$. Matrix elements $(c_1 \mid \mathscr{H}_{Av} \mid F)$ are tabulated as M_{12} integrals. Matrix elements of $\mathscr{H}_0 - \mathscr{H}_{Av}$ are two-electron integrals arising from interactions with the open shells of the reference target configuration. They reduce to M_{23} integrals with coefficients that depend on m_s and m_l quantum numbers, obtained as in KDB.

The rectangular matrix $M_{\mu,ip}$ is constructed by rows: given μ, all values of open-channel indices p are considered in order, with elements $i = 0, 1$ computed and stored successively for each p. Each row in turn is output to auxiliary storage by CON/360. Since index μ has the dimension of the $N + 1$-electron Hilbert space, $M_{\mu,ip}$ will in general be too large for storage in available main memory of a computer.

The M_{23} integral blocks (minor segments of the transformed integral table produced by ORTHSCAT) are treated as pages in a demand paging algorithm. Any block, once read into main memory, is kept until no space remains. Then the paging system is reset, and built up again as blocks are required. Individual integrals are located within the blocks by Eq. (87).

Elements of the free–free matrix are computed by program module FFMAT. The matrix elements, defined by Eqs. (21) and (12) are

$$M_{ij}^{pq} = (\Theta_{ip} \mid H - E \mid \Theta_{jq}) \tag{105}$$

$$= \sum_{\sigma} \sum_{\tau} c_\sigma{}^{p} (\Phi_\sigma^{ip} \mid H - E \mid \Phi_\tau^{jq})\, c_\tau{}^{q}. \tag{106}$$

FFMAT follows procedures very similar to those of BFMAT, both modelled on KDB. Because the free–free matrix is a square matrix of linear dimension only twice the number of open channels, it is stored in main memory. Coefficients $\{c_\sigma{}^p\}$ and the corresponding list of N-electron determinants $\{\Phi_\sigma\}_p$ are available as data stored by the target atom programs.

Because open-channel orbitals F_{jq} are not quadratically integrable, matrix elements M_{ij}^{pq} are not defined unless

$$\tfrac{1}{2}k_q{}^2 = E - E_q = \epsilon_q\,, \tag{107}$$

where k_q is the parameter used to define the asymptotic behavior of F_{jq}, and E_q is an eigenvalue of the target configuration atom interaction matrix,

$$(\Theta_p \mid H \mid \Theta_q) = E_q \delta_{pq}\,. \tag{108}$$

From Eqs. (9), (12), and (13), the antisymmetrized $N + 1$-electron functions Θ_{jq} can be written in the form

$$\Theta_{jq} = \mathcal{A}\Theta_q F_{jq}\,. \tag{109}$$

If this is substituted into Eq. (105), making use of Eq. (107), M_{ij}^{pq} can be written in the form

$$M_{ij}^{pq} = (\Theta_p \mid H - E_q \mid \Theta_q)(F_{ip} \mid F_{jq}) + [\Theta_{ip} \mid H - \epsilon_q \mid \Theta_{jq}]. \tag{110}$$

Here the square-bracket notation is used to denote a matrix element evaluated *as if* $(F_{ip} \mid F_{jq})$ were zero for all values of the indices ip, jq. Terms in $(F_{ip} \mid F_{jq})$ are explicitly collected together in the first term of Eq. (110), which vanishes in consequence of Eq. (108), regardless of the definition of $(F_{ip} \mid F_{jq})$. A more precise argument can be based on truncating all integrals at some large value of the radial variable r, then passing to the limit $r \to \infty$. The result is

$$M_{ij}^{pq} = [\Theta_{ip} \mid H - \epsilon_q \mid \Theta_{jq}] \tag{111}$$

$$= \sum_{\sigma} \sum_{\tau} c_{\sigma}{}^{p} [\Phi_{\sigma}^{ip} \mid H - \epsilon_q \mid \Phi_{\tau}^{jq}] \, c_{\tau}{}^{q}. \tag{112}$$

Matrix elements $[\Phi_{\sigma}^{ip} \mid H - \epsilon_q \mid \Phi_{\tau}^{jq}]$ are obtained in FFMAT by applying the KDB algorithm to the determinant codes for Φ_{σ} and Φ_{τ}, then appending $(l\,n\,s\,m)_p$, $(l\,n\,s\,m)_q$ to the relative excitation code of Φ_{σ} with respect to Φ_{τ}. If this relative excitation index is denoted by Δn, the only nonvanishing matrix elements are of the form:

$$\Delta n = 0; \qquad \pm(F_{ip} \mid \mathscr{H}_{\sigma} - \epsilon_q \mid F_{jq}), \tag{113}$$

$$\Delta n = 1; \qquad \pm(c_1 F_{ip} \mid R \mid c_2 F_{jq}), \tag{114}$$

where c_a denotes a bound orbital.

The further analysis of these matrix elements by FFMAT follows the pattern of KDB and BFMAT. For $\Delta n = 1$, $(cF \mid R \mid cF)$ reduces to a sum of M_{21} and M_{22} integrals multiplied by products of Gaunt coefficients. For $\Delta n = 0$, matrix elements $(F \mid \mathscr{H}_{Av} - \epsilon \mid F)$ are tabulated as M_{11} integrals, and matrix elements $(F \mid \mathscr{H}_{\sigma} - \mathscr{H}_{Av} \mid F)$ are sums of M_{21} and M_{22} integrals.

The matrix M_{ij}^{pq} is separated into four blocks M_{00}^{pq}, M_{01}^{pq}, M_{10}^{pq}, and M_{11}^{pq}, since these blocks are manipulated separately in several variants of the multichannel variational method. These matrices are constructed and stored in main memory.

The M_{11}, M_{21}, and M_{22} integral blocks required by FFMAT are treated as pages in a demand paging algorithm, as in BFMAT. Individual integrals are located within the blocks by the formulas of Eqs. (76), (82), and (85).

The four integrals indexed by (ij), with other indices equal, are stored together in the integral blocks M_{11}, M_{21}, and M_{22} with the ordering convention denoted by $\{ij\}$ in Eqs. (76), (82), and (85). This ordering convention, which is the natural counting order of indices for M_{21}, is imposed on M_{11} and M_{22} in order to standardize the table look-up logic of FFMAT, which combines integrals from these three different blocks. The ordering $\{ij\}$ ensures that indexing (i, j) depends only on information supplied by the free orbital codes $(l\,n\,s\,m)_p$, $(l\,n\,s\,m)_q$ regardless of permutations of indices carried out by table look-up algorithms for the various integrals.

H. *Construction of* m_{ij}^{pq} (TMAT, VTRAN, MMAT)

The matrix m_{ij}^{pq}, defined by Eq. (18), is constructed indirectly by means of a triangular decomposition of the bound–bound matrix

$$M_{\mu\nu} = H_{\mu\nu} - E\delta_{\mu\nu} . \tag{115}$$

In possible applications of the present method the linear dimension of this matrix, which is the dimension of the $N + 1$-electron Hilbert space, may be several thousand, so the matrix may have more than ten million independent elements. Direct evaluation of the inverse matrix, as required for direct evaluation of Eq. (18), would be a formidable task.

This task is made tractable by an algorithm [19] that adapts the well known Cholesky decomposition to the Hermitian but not positive definite matrix $M_{\mu\nu}$. A lower triangular matrix $T_{\mu\alpha}$ is defined by

$$M_{\mu\nu} = \sum_{\alpha} T_{\mu\alpha}\sigma_{\alpha}T_{\alpha\nu}^{\dagger} , \tag{116}$$

where σ_α is a diagonal matrix with elements ± 1. All matrix elements here are real. For a real matrix $T_{\alpha\nu}$ the adjoint $T_{\alpha\nu}^{\dagger}$ is just the transposed matrix. Program module TMAT constructs $T_{\mu\alpha}$ by an algorithm that permits sequential data processing of both $M_{\mu\nu}$ (stored as a lower triangle) and of $T_{\mu\alpha}$. The matrix σ_α is represented by a list of integer index pointers to the relatively small number of elements $\sigma_\alpha = -1$. This number, n_σ, is the number of negative eigenvalues of $M_{\mu\nu}$. When $M_{\mu\nu}$ can be contained in main computer memory, it is replaced element by element by $T_{\mu\nu}$. Otherwise, main memory is used as a buffer area and $T_{\mu\nu}$ is built up in sequential segments [19].

Program module VTRAN constructs an auxiliary rectangular matrix $B_{\alpha,ip}$ such that

$$\sum_{\sigma} T_{\mu\alpha}B_{\alpha,ip} = M_{\mu,ip} \tag{117}$$

or

$$B_{\alpha,ip} = \sum_{\mu} (T^{-1})_{\alpha\mu}\, M_{\mu,ip} \tag{118}$$

where $M_{\mu,ip}$ is the bound–free matrix. Because T is triangular, B can be constructed by sequential processing of both $T_{\mu\alpha}$ and $M_{\mu,ip}$. In general, both of these matrices can be too large for storage in main computer memory. When $M_{\mu,ip}$ can be contained in main memory, it is replaced element by element by $B_{\alpha,ip}$. Otherwise, main memory is used as a buffer area and $B_{\alpha,ip}$ is built up in sequential segments [19].

In terms of the auxiliary matrix B, Eq. (18) reduces to

$$\begin{aligned} m_{ij}^{pq} &= M_{ij}^{pq} - \sum_{\alpha} B_{ip,\alpha}^{\dagger} \sigma B_{\alpha,jq} \\ &= M_{ij}^{pq} - \sum_{\alpha} \sigma_{\alpha} B_{\alpha,ip} B_{\alpha,jq} \,. \end{aligned} \tag{119}$$

This sum is evaluated by program module MMAT in a single sequential scan of matrix $B_{\alpha,ip}$. The relatively small free–free matrix M_{ij}^{pq} is stored in main memory and converted in place to m_{ij}^{pq}.

The free-orbital normalization indicated by Eqs. (70) is maintained until the completion of MMAT. Then factors $(k_p k_q)^{-1/2}$ are introduced by the subsequent program RMAT in order to convert m_{ij}^{pq} to the normalization specified by Eqs.(8).

I. *Computation of the Reactance Matrix* (RMAT)

Program module RMAT uses the *optimized anomaly-free* (OAF) variational method to compute the reactance matrix K_{pq} or R_{pq}. This method, which is described in detail elsewhere [2], is the most satisfactory of a number of alternative methods based on the multichannel Kohn variational principle [10].

The transformation of m_{ij}^{pq} to upper triangular form, indicated in Eqs. (35) and (36), is carried out by the double QR algorithm [20]. This algorithm is modified so that complex eigenvalues lead to real but irreducible 2 × 2 blocks along the diagonal of the transformed matrix m'. With this provision, all numbers are real, and the transformation u is an orthogonal matrix. The triangularization algorithm originally published [2], an extension of the Jacobi method, was found not always to converge in cases of closely spaced eigenvalues, whereas the convergence of the QR algorithm is assured [20].

The QR algorithm does not guarantee that diagonal elements of the transformed matrix (eigenvalues if no complex roots occur) are ordered by magnitude. An additional series of 2 × 2 rotations of adjacent rows and columns are carried out by RMAT to convert to m' to a canonical form. If there are no complex eigenvalue pairs, this form is such that $m'_{10} = 0$; m'_{01} is nonsingular with its largest elements arranged along the leading diagonal; and for each such element, the corresponding diagonal element of m'_{00} is less in magnitude than the corresponding diagonal element of m'_{11}. In the case of complex eigenvalues, nonzero elements are necessarily left in m'_{10}. In this case, Eq. (39) is replaced by [2]

$$[K'] = -(m'_{01} - m'^{\dagger}_{10})^{-1} m'_{00} \,. \tag{120}$$

The K matrix is computed from Eq. (40). This computed matrix is not in general symmetric. The degree of asymmetry serves as a criterion for convergence of the overall calculation. The symmetric part of K is diagonalized to produce eigenphases and eigenchannel vectors. This information is recombined to give physical inelastic and elastic cross sections, using Eq. (30).

J. *Resonance Search* (SCATRES)

A multichannel resonance search procedure, which has been fully described elsewhere [2], is included as an optional modification of the outer loop module CISCAT.

4. APPLICATIONS AND DISCUSSION

The method described here has been applied to a series of electron-atom scattering calculations of increasing complexity. These calculations have served to establish the validity and limitations of the method and of the system of computer programs that embody the algorithms described here.

Calculations have been reported on e^--H resonances in the elastic region [21], of e^--He elastic scattering, including the isolated resonance near 19.3 eV [22], of e^--Li, Na, K elastic scattering and resonances [23], and of e^--He inelastic scattering, in the energy region of excitation of $n = 2$ states [24]. Calculations of electron scattering by C, N, and O atoms are currently in progress.

Results obtained are in substantial agreement with the best previous theoretical calculations and with available experimental data in all these applications. In calculations of e^--He inelastic scattering, the 2^3S excitation cross section has been obtained in qualitative agreement with experimental data for the first time. The most elaborate previous calculations had to be modified by an *ad hoc* adjustment of the 2^3S excitation cross section in order to be compared with experiment [25].

The most severe limitations of the present method arise from the particular choice of functional forms made in the implementation described here. The choice of spherical Bessel functions as free basis orbitals limits applications to scattering by neutral atoms, since Coulomb wave functions are needed to describe electron–ion scattering. By itself, this limitation could be removed by developing efficient quadrature techniques for integrals representing the generalization to Coulomb wave functions of those indicated in Eqs. (73). Analytic methods for these integrals have been proposed [26], but a comparative study of efficiency is not yet available.

A more fundamental limitation is due to the fact that the effective potentials in electron–atom scattering, arising from static multipole moments or from multipole polarization of the target atom, can be of very long range. Wave functions are modified from their far asymptotic forms by terms of the form of oscillatory functions divided by powers of r [27]. Such functions, when included in the basis set of normalizable orbitals, have been found to be essential to rapid convergence of the orbital expansion in variational calculations [28]. Since such damped oscillatory functions are necessarily energy-dependent, their inclusion would require reconstruction of the bound–bound matrix at each reference channel k-value. It would also increase the number of independent basis functions required in a multichannel problem. However, without such functions, convergence of the orbital expansion is slow and irregular.

Inclusion of asymptotic functions determined by numerical integration would be desirable, but requires either a basic reformulation of the method [5, 29] or the development of new, highly efficient methods for numerical evaluation of matrix elements involving oscillatory functions.

Eigenfunctions of $\mathbf{L}^2$ and $\mathbf{S}^2$ are *not* constructed explicitly in the method described here. This causes matrices occurring in applications to be unnecessarily large, with redundant elements. This obvious inefficiency has been accepted only as a temporary expedient, in order to arrive more quickly at a working program capable of testing the general method. Several procedures are available for utilizing LS-eigenfunctions throughout the calculations, but considerable problems of program organization are encountered in implementing any such procedure without imposing limitations on target atom shell structure or on the allowed range of angular quantum numbers and virtual excitations.

A computer program constructed according to the algorithms described here has been used for the various applications mentioned above. Some idea of the computational requirements of this method can be obtained from the time and space parameters of typical production runs for e-He inelastic scattering, on an IBM 360/195 system, using 3330 disk units. For S-states, with 12 open channels and 5 distinct k-values, a run at one total energy with 8 s-orbitals and 6 p-orbitals in the normalizable basis required $256K$ bytes of main memory and ran in 110 seconds CPU time. Disk space of 100 cylinders was allocated but only used in part. For D-states, with 16 open channels and 5 distinct k-values, a run at one energy with 8 basis s-orbitals, 6 p-orbitals, 6 d-orbitals, and 5 f-orbitals required $384K$ bytes of main memory and 22 minutes CPU time. Disk space of 100 cylinders was allocated.

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