Numerical methods every atomic and molecular theorist should know

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Abstract | This Technical Review encapsulates the methods and numerical techniques that have been so successfully used over the years to study the electron scattering of atoms and molecules. In the past few decades, these approaches have also proven effective in treating the time-dependent interaction of strong electromagnetic fields with atoms and molecules. There are clear synergies between the two that can be exploited computationally. The ideas discussed in this Technical Review have played an important role in shaping modern atomic and molecular physics, and we expect that future developments will build heavily on these foundations.

Self-consistent field
It is often synonymous with the Hartree–Fock method and mean-field method. It is based on Douglas Hartree's assumption that each particle in an N-body system could be treated in the average field of the other $N-1$ particles of the system.

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Our ability to compute the ground- state and excited-state energies of atoms and molecules, as well as electron–atom and electron–molecule collision cross-sections, is central to understanding the quantum mechanical nature of matter. The theoretical foundations of atomic, molecular and optical (AMO) physics are derived by combining classical electromagnetic theory and quantum mechanics. In contrast to nuclear and particle physics, the forces involved in AMO theory are well known. This led to an early development of theoretical and computational methods to accurately solve the Schrödinger equation and made the comparison of these methods to one another and to experiments possible. In addition, the development of alternative computational methods enabled the assessment of numerical uncertainties and in many instances the actual prediction of experimental outcomes, which might be difficult or impossible to perform in practice. The data derived from calculations are often required in other branches of physics, such as modelling astrophysical phenomena or fusion plasmas, and lighting devices. In this Technical Review, we discuss and compare a number of the existing numerical methods used in AMO physics.

Early history

Atomic and molecular structure. Most of computational AMO physics has its roots in developments that started only shortly after the discovery of the Schrödinger equation. The early pioneers used a variety of approaches to understand the structure of atoms and how atoms come together and form chemical bonds. The concept of the self-consistent field was put forward by Douglas Rayner Hartree[1,2], John Clarke Slater[3], Vladimir Fock[4] and others (see REF.[5] for a historical perspective). Its extension to include exchange effects, as in the Hartree–Fock equations, was first solved for atoms using numerical techniques developed to approximate

differential equations by difference equations on an analogue computer called the differential analyser[6]. In such calculations, each electron moves in the average field (self-consistent field) produced by the other electrons and the instantaneous electron–electron interaction (correlation) of the particles is neglected.

The initial approach to computationally solve the integro-differential Hartree–Fock equations used finite-difference methods on a discrete grid. Although the required numerical calculations were labourious, they were still possible using the hand calculators available at the time. In the early 1950s, a new method to tackle molecular calculations was independently pioneered by Clemens C. J. Roothaan[7] and George G. Hall[8]. With it, it became possible to solve the self-consistent field equations by approximating the atomic orbitals as linear combinations of analytic functions such as exponentials (Slater orbitals). The development of digital computers around the same time lead to widespread use of Hartree–Fock computations for atomic, molecular and nuclear systems[9–13].

Radial integrals are used for forming the matrix elements of the Hamiltonian. For atoms, they can be computed using semi-analytic numerical techniques that result in reducing the problem to the solution of a matrix-eigenvalue problem. However, the lack of spherical symmetry in molecules does not straightforwardly afford the reduction of the problem to one-dimensional radial equations. Nonetheless, once it became clear that atomic orbitals can be approximated by linear combinations of simpler functions, the methods developed for atoms could be generalized for molecules, albeit with a more complex numerical procedure to compute the integrals.

Parallel to the development of the self-consistent field methods, other researchers[14–19] were pursuing an alternative numerical treatment of He and H_2. They abandoned

Key points

- We overview the best-of-breed numerical methods being used to compute electron–atom and electron–molecule scattering cross-sections and to propagate the Schrödinger equation in time.
- We describe the close-coupling, R-matrix and Kohn variational methods and briefly discuss the importance of complex scaling to practical scattering theory.
- We outline how these techniques may be extended to treat the time-dependent Schrödinger equation.

Variational principle
A principle used in the calculus of variations concerned with finding functions that minimize, maximize or make stationary quantities defined by differential of integral equations.

Configuration interaction
A quantum chemical variational method for solving the Schrödinger equation of many-body systems. It relies on constructing linear combinations of Slater determinants of fixed spin orbitals. The unknown linear coefficients are computed using the Rayleigh–Ritz variational principle. In theory, the method is exact, but in practice, the computational limitations arising from a large number of configurations force the truncation of the expansions.

R-matrix
The R-matrix relates the channel wavefunction F_c to its derivative F'_c at the R-matrix boundary $r = a_0$ by the equation: $\mathbf{F} = \mathcal{R} \mathbf{F}'$, where the labels on the elements of the matrix refer to channels, c.

the concept of a single orbital for each electron and expanded the wavefunction of both electrons using physically motivated analytic forms containing parameters optimized by the variational principle. This idea led to extremely accurate treatments of both He and H_2. These early calculations were also performed by hand or using mechanical calculators. A number of these early calculations explicitly included terms containing the inter-electronic distance in the variational wavefunction and required the calculation of matrix elements that rapidly become quite expensive to compute with a growing system size. Nonetheless, some works pushed the basic ideas even to calculations with as many as four electrons[20–24].

The idea of using more than a single orbital for each electron may be generalized naturally, leading to the construction of a set of configurations that may then be superposed using the variational principle to obtain the optimal energy. This approach, termed configuration interaction (for very early applications, see REFS[25,26], and for a historical overview, see REF.[27]), remains today[28,29] one the more accurate numerical approaches for the calculation of the ground and excited states of small molecules.

The insight gained and the methodologies developed have been refined over many decades and with the advent of modern computing technology led to our current ability to accurately compute the ground and even the excited states of fairly complex molecules and materials.

Atomic collisions. It is perhaps a bit less known that in the early 1930s there were parallel efforts to describe the collisions of electrons with atoms and simple molecules[30–32]. At the time, it had already become clear that approximations such as those developed by Max Born and J. Robert Oppenheimer[33] would fail for slow electrons where the wavefunction deviated strongly from a plane wave form. The use of the differential analyser enabled calculations of the cross-sections for low-energy scattering of electrons from the He atom[32].

For scattering processes, there is no variational principle guaranteeing that some quantity, such as the phase shift, would satisfy a minimum principle. Nevertheless, methods very similar to the numerical integration and variational techniques used for bound states can be applied with considerable success to collisions[34–39]. Variational principles were eventually developed applicable to both electron and heavy particle collision problems. Variants of these methods are are still in use today (see REF.[40] for a thorough discussion).

Electron correlations

Mean-field methods can give a broad picture of electron motion in atoms and molecules, but electron correlation is responsible for other important phenomena observed in molecular systems. This is evident in quantum chemistry where it is essential to obtain the quantitative details of a potential energy surface correctly to understand the molecular dynamics. Similarly, to accurately predict atomic and molecular spectra, photo processes and electron collision cross-sections, the understanding of electron correlation is critical. But this is not easy because multiple electronic states come into play and ways to balance the treatments of electron correlation in systems involving significant changes from their initial configuration are needed.

Numerical methods are also important in the context of modelling of astrophysical, fusion and lighting plasmas. Experiments cannot supply the data needed for this modelling due to time limitations and systems inaccessible in the laboratory. Reliable theoretical and computational methods provide a cheaper alternative, but for the obtained data to be meaningful it is necessary to control the errors present in the calculation.

In this Technical Review, we selected only a few of the many methods that have been developed over the past few decades to treat systems in the continuum. The close-coupling, R-matrix and Kohn variational methods have proven their robustness. In conjunction with the method known as complex scaling, it has been possible to accurately solve problems thought to be intractable for many years.

The key ideas we introduce here provided the foundations for more recent developments involving the interaction of short, intense radiation with atoms and molecules. They enabled the exploration of atomic and molecular systems on timescales comparable to the motion of the electrons in these systems and even to manipulate them to control the outcome of chemical reactions[41,42]. In this case, the problem is actually time dependent, a further complexity, but to understand how these electromagnetic fields can control the electronic motion in molecular systems, the methods and numerical techniques developed by time-independent collision theory are needed. Our ability to control the electrons on their natural attosecond timescale has vastly increased our understanding of the way electrons behave in molecules, enabling studies of processes such as the time delays of photoejection, double ionization and how charge migration unfolds in polyatomic systems.

Discretization of space

Basic to all numerical solutions of the Schrödinger equation is the need to discretize the spatial coordinates and to impose appropriate boundary conditions. Many of the details of the discretization and boundary conditions depend on whether the problem is approached as a partial differential equation or the formally equivalent integral equation. There are essentially three ways to discretize the spatial coordinates: finite difference (FD)[43], a basis set expansion (spectral)[44] or the use of numerical quadrature[45]. By adopting an integral equation formalism, it is easier to impose the boundary conditions

from the outset. This leads to more stable numerics since the required solution is already determined at the end points. In addition, numerical integration is always more stable than numerical differentiation.

The first two approaches have roots in the methods discussed in the previous section. Serious use of integral equations began in the 1970s[46–53] and variants of the original methodology still exist. Basis set expansions may be defined globally or over a set of subdomains (finite elements (FE))[54–59] that are linked together by continuity conditions. Under certain mathematical conditions, such as no derivatives above the second order, only function continuity is sufficient. FD approaches are particularly easy to program, but have issues of accuracy if the order of the FD is too low. Higher-order FD methods can often compete successfully with spectral and FE techniques and deserve consideration when constructing an accurate and efficient spatial discretization.

Most numerical codes tend to use either FD, spectral, FE or integral equation methods, but recent implementations have successfully used mixtures of these to optimize the efficiency and accuracy of the numerical results[60–64].

FD approaches most naturally appear in solutions of coupled differential and integro-differential equations. Spectral and FE methods are more naturally rooted in variational approaches but the boundaries are not sharp. Integral equation formulations can easily replace the differential equations using well-established methods[50] where the FDs are replaced by numerical quadrature using a Green's function. Using differential or integral equations is often a matter of choice and a trade-off between simplicity and accuracy.

When these various approaches are used to solve the time-independent Schrödinger equation, the initial partial differential equations are reduced to a set of algebraic equations[50,65,66]. In the time-dependent case, the partial differential equations are reduced to a set of coupled, time-dependent algebraic equations. The structure of the equations is very dependent on the method of discretization. FD and FE methods can often lead to sparsity in the equations, but in the case of identical fermions, the presence of exchange terms can destroy that sparsity. For variational methods, where global basis set expansions tend to be used, typically there is no sparsity.

In this Technical Review, we discuss how these different spatial discretization techniques are integrated into the solution of the Schrödinger equation for atomic collision problems. We also cover the way in which these methods are incorporated into the time-dependent Schrödinger equation.

Expansion of the collision wavefunction

One of the earliest techniques used to solve the Schrödinger equation for the collision of electrons with atoms, the close-coupling (CC) method[67–70], uses an expansion of the collision wavefunction Ψ of the form

$$\Psi = \sum_{c=1}^{N} \mathscr{A}\left[\psi_c(\mathbf{x}_1 \cdots \mathbf{x}_N) F_c(\mathbf{x}_{N+1})\right] \quad (1)$$

where ψ_c is a state of the N electron target atom (with x_k representing the coordinates of the kth electron, including its spatial coordinates and its spin properties) and F_c, the unknown channel function that is antisymmetrized into ψ_c as indicated by the $\mathscr{A}$ symbol. The separation of the unknown collision wavefunction into the product of a known target wavefunction times an unknown collisional wavefunction is common to almost all of the theoretical collision methods.

Inserting equation 1 into the Schrödinger equation, and then multiplying successively by ψ_c and integrating over the target coordinates, leads to a set of coupled, integro-differential equations of the general form

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 - E_c\right)F_c(\mathbf{r}) + \int \sum_{c'} V_{c,c'}(\mathbf{r},\mathbf{r}')F_{c'}(\mathbf{r}')\mathrm{d}\mathbf{r}' = 0 \quad (2)$$

where

$$V_{c,c'}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')U_{c,c'}(\mathbf{r}) + K_{c,c'}(\mathbf{r},\mathbf{r}') \quad (3)$$

Here, E_c is the channel energy, $U_{c,c'}$ is the local part of the interaction potential consisting of the electrostatic interaction of the scattering electron with the nucleus and the other electrons whereas $K_{c,c'}$ is a general non-local interaction due to electron exchange and correlation. $U_{c,c'}$ can be long-range whereas $K_{c,c'}$ is short range and typically vanishes rapidly as the separation between $\mathbf{r}$ and $\mathbf{r}'$ increases. Here, $\mathbf{r}$ and $\mathbf{r}'$ refer to the spatial coordinates of electrons in the system.

The unknown functions F_c in equation 2 may be further expanded in a series of spherical harmonics, leading to a larger set of coupled equations, but in a single radial variable. The non-local kernel, K, often has a special structure that can be exploited in the solution of the equations. A short discussion on the numerical methods used to solve the radial CC equations is provided in BOXES 1 and 2.

Box 1 | Solution of radial close-coupling equations

In the numerical solution of the radial integro-differential equations, there are typically three major steps. Near $r = 0$, the solutions are expanded in a power series and the coefficients determined by matching. Since the equations are second order, two starting values are need to continue the solution to larger radial values. The most used approach has been the Numerov method since the equations do not contain a first-order derivative. The Numerov method achieves fourth-order accuracy using three points, which is better than the standard three-point finite difference method.

The presence of the exchange terms suggests that an iterative solution is needed. However, by suitably rearranging the exchange terms, the equations may be rewritten so that exchange is separated into a term that may computed using outward integration plus an inhomogeneity. After the equations for the homogeneous and inhomogeneous terms are computed they may be combined to form the desired solution. In practice, this leads to a larger set of coupled differential equations that are integrated outward until the exchange vanishes and the solutions can be matched to free waves or connected to an asymptotic expansion. The asymptotic expansion has the merits that it avoids the mixing of exponentially growing solutions for closed channels. Other techniques such as R-matrix propagation or inward integration have also been used in practical calculations[94].

Another approach, which has significant merit, is to convert the integro-differential equation into integral equations. These equations are initially of the Fredholm form. Introducing quadratures converts them into a set a linear algebraic equations that may be solved using standard techniques. Although these Fredholm equations are unconditionally stable, they can be expensive to solve, as the matrices can become quite large in realistic problems. Alternatively, the Fredholm equations may be converted into a larger set of inhomogeneous, Volterra equations and solved by outward numerical integration. This is illustrated in the example in BOX 2.

Box 2 | Fredholm to Volterra integral equations

Consider the following Fredholm integral equation of the second kind

$$u(r) = \sin(kr) + \mathbf{L}(r)u(r) \tag{30a}$$

$$\mathbf{L}(r)u(r) = \int_0^\infty G(r|r')V(r')u(r')dr' \tag{30b}$$

$$u(r) = \sin(kr) + \cos(kr)\int_0^r \sin(kr')V(r')u(r')dr' + \sin(kr)\int_r^\infty \cos(kr')V(r')u(r')dr' \tag{30c}$$

Introduction of quadratures directly into equation 30a would reduce the Fredholm integral equation to a set of linear equations that could be solved by a number of well-known techniques. However, the derivative singularity in equation 30a can lead to slow convergence. Under such conditions, using a higher-order quadrature formula does not guarantee better accuracy or more rapid convergence. To avoid these pitfalls, equation 30a is rewritten as

$$u(r) = \sin(kr) + \mathbf{L}_0(r)u(r) + \sin(kr)\int_0^\infty \cos(kr)V(r)u(r)dr \tag{31}$$

$$\mathbf{L}_0(r)u(r) = \cos(kr)\int_0^r \sin(kr')V(r')u(r')dr' - \sin(kr)\int_0^r \cos(kr')V(r')u(r')dr' \tag{31b}$$

The important point to note about the action of $\mathbf{L}_0$ on the unknown solution is that due to the symmetry of the operator, a numerical quadrature can be chosen that only requires knowledge of the solution at previously determined values. Consequently, the integrals may be computed recursively. Thus, once the solution to the equation

$$u_0(r) = \sin(kr) + \cos(kr)\int_0^r \sin(kr')V(r')u_0(r')dr' - \sin(kr)\int_0^r \cos(kr')V(r')u_0(r')dr' \tag{32}$$

is determined, the solution to u is

$$u(r) = u_0(r)[1+c]\; ;\;\; c = \frac{c_0}{1-c_0},\;\; c_0 = \int_0^\infty \cos(kr)V(r)u_0(r)dr \tag{33}$$

This approach generalizes to the case of non-local potentials of the form

$$U(r|r') = \sum_i u_i(r)\phi_i(r') \tag{34}$$

The solutions to an augmented set of Volterra equations may be linearly combined to form the total solution from a set of easily computed integrals and some straightforward linear algebra.

There is a generalization of equation 1, to be discussed later

$$\Psi = \sum_{c=1}^N \mathscr{A}\left[\psi_c(\mathbf{x}_1, \mathbf{x}_2 \cdots \mathbf{x}_N)F_c(\mathbf{x}_{N+1})\right] + \sum_{q=1}^M b_q \chi_q(\mathbf{x}_1, \mathbf{x}_2 \cdots \mathbf{x}_{N+1}) \tag{4}$$

The b_q are variational parameters and χ_q terms in the second summation above are chosen so that this entire term vanishes as the electron coordinate goes to ∞. This term is designed to account for correlation between the target and incident electron at short range that are absent from the CC expansion. The individual terms in the expansion are often called pseudo-states to distinguish them from the actual target states in the first summation. This is not an optimal approach as it has serious disadvantages for re-arrangement collisions.

Re-arrangement collisions
These are collisions in which the initial and final states are eigenstates of different unperturbed Hamiltonians.

Consider a simple case where an electron collides with an atom with an energy sufficient to excite and ionize the target. If one restricts the first term in the expansion to only a finite set of neutral target states, it is impossible to precisely describe ionization using a finite set of pseudo-states. A properly chosen set of pseudo-states have been shown to approximate excitation to the ionization continuum not accounted for in the standard CC expansion. However, the use of pseudo-states also has several difficulties. Since they mathematically can mimic a pseudo-target state plus a captured electron, when the electron energy is sufficiently large to excite that target, artificial resonances can appear. In addition, the way to use them to actually compute impact ionization cross-sections is also a matter that requires consideration.

To better account for ionization, it is necessary to either include continuum target states or ionic channels in the expansion or develop a more complete CC method that can account for ionization in a more rigorous manner. Either approach is numerically difficult, but there has been good progress. The convergent CC (CCC) method and the use of exterior complex scaling (ECS) have been developed to overcome these difficulties, but by entirely different approaches. ECS uses some elegant mathematics to turn the continuum problem into an $\mathscr{L}^2$ problem. This is accomplished by replacing the real radial coordinate with a complex variable outside the interaction region. It becomes possible to extract the required cross-sections using either flux or surface integral techniques. We will discuss ECS in more detail in the next section. The CCC method demonstrated that by using enough of a complete set of properly defined discrete states, it is possible to avoid the pseudo-resonances and to extract the differential impact ionization cross-sections[71,72]. In the CCC method, the CC equations are converted to integral equations in momentum space, discretized via quadratures and then solved using fairly standard linear systems methods. Extensive use of parallel programming methods make this possible and efficient on modern supercomputers.

An accurate representation of the collision complex, that is, the target and break-up channels, can have a profound effect on the ability of any given method to accurately predict collisional properties. To a large degree, this is simply a restatement of the difficulties always encountered in balancing the correlation of quantum mechanical systems made up of many identical particles.

Complex scaling. The method of complex scaling has, in one form or another, been successfully used to solve some otherwise intractable problems in atomic and molecular physics[73]. The original idea, developed by the mathematician Barry Simon[74], was to rotate all the electronic coordinates by a complex phase factor θ as $r \to r\exp(i\theta)$.

Since the rotated wavefunction decays exponentially, it is natural to apply standard bound-state variational methods to compute the resonances. Although this works for simple systems, it was soon discovered that

Preconditioner
In this context, it refers to a matrix transformation of a set of linear equations that are more suitable for finding a solution by iterative techniques.

it leads to difficulties, in that the most tightly bound electrons oscillate rapidly and these oscillations are difficult to capture variationally. In addition, for many problems, uniform complex scaling cannot be applied as the potential is non-analytic over the entire rotated coordinate.

To circumvent such problems, it was proposed that the complex scaling should be performed only outside the molecular interaction zone, R_0, where the potential has no pathologies[75]. This ECS can be done abruptly or smoothly, where the transition from real to complex coordinates is performed over a small interval near R_0. There are a significant number of papers[76–78] in the literature showing how one can effectively implement ECS for atomic and molecular scattering problems and problems involving external fields.

There are connections to complex absorbing potentials, but in this Technical Review we will restrict ourselves to a few remarks. Typically, abrupt ECS is performed using the transformation

$$r \rightarrow R(r) = \begin{cases} r & r < R_0 \\ R_0 + (r - R_0)e^{\lambda + i\eta} & r > R_0 \end{cases} \quad (5)$$

where λ and η are arbitrary parameters to perform the scaling. In smooth exterior complex scaling, one uses a transformation such as

$$r \rightarrow \phi(r) = r + \lambda g(r)$$
$$\lambda = \exp(i\theta) - 1$$
$$g(r) = \begin{cases} 0 & r < R_0 \\ (r - R_0)[1 - \exp - \eta(r - R_0)^2] & r > R_0 \end{cases} \quad (6)$$

If a complete basis set expansion is used to solve the Schrödinger equation, the exact solution is independent of θ and η. In numerical calculations, θ may also be used as a variational parameter to minimize the complex energy.

In both abrupt and smooth ECS, the Hamiltonian remains unchanged for $r < R_0$. The method leaves the bound-state spectrum unchanged, but the continuum states now exponentially decay. Thus, variational methods that use only $\mathscr{L}^2$ functions may be used. It is also possible to use grid-based approaches with FD or FE. ECS has also been extended to time-dependent problems. Note that infinite-range smooth ECS can be shown to be equivalent to the introduction of a perfect absorbing potential and has been used quite successfully in a number of important applications[76–78].

One notable success of the approach has been its application to computing impact ionization amplitudes for electrons on the hydrogen atom[73]. This application required the iterative solution of a large, sparse set of complex linear equations. This could only be accomplished by finding a suitable preconditioner. To find a good preconditioner, direct methods, such as SuperLU[79], are used with a low order, but less accurate FD approximation to the problem. This is then used as a preconditioner for the full, higher-order FD method to solve the exact set of linear equations iteratively.

The R-matrix method. As mentioned earlier, the reduction of the collision problem to the solution of a set of integro-differential or, alternatively, integral equations, is not an optimal numerical approach. Other procedures, such as those used in quantum chemistry, which convert the collision problem to one involving the manipulation of matrices, are more flexible and easier to use numerically. One of the first such approaches, which has its roots in nuclear physics[80–82], is the R-matrix method (see BOX 3 for the detailed theoretical formulation of the R-matrix method). In the R-matrix method, the CC expansion is augmented by a set of square integrable terms and the collision term is expanded in a set of known analytic or numerical functions, u_{ci}^0, inside a finite radius $r \le a$. It is assumed that exchange vanishes beyond $r \le a$ region and only local interactions remain.

By diagonalizing the Schrödinger equation in this internal region ($r \le a$), one obtains a set of discrete states that may be used to expand the collision wavefunction at any arbitrary energy. This is a significant advantage in that a single, but often expensive, computational step enables the problem to be solved at many energies. The first applications of the R-matrix in AMO physics was to calculate the electron scattering off atoms and

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Box 3 | Quick R-matrix numerical tutorial

The internal region
Solving equation 9 is often the major computational effort in R-matrix calculations. To accomplish that, one needs needs to compute the Hamiltonian matrices of the operator $[H_{N+1}(r;R) + L_{N+1}]$. Much of the effort dedicated to this is quite similar to a standard bound-state eigenvalue problem; one- and two-electron integrals must be computed and the Hamiltonian matrices assembled. For atomic R-matrix calculations, the most accurate approach is based on using B-splines as a radial basis and using a non-orthogonal set of configurations[103,166]. This variant of the R-matrix enables the target states to be computed very accurately with compact configuration interaction expansions. In addition, using a B-spline radial basis provides a great deal of flexibility in the representation of the scattering functions.

The external region: R-matrix propagation. The R-matrix propagation approach can be used to extend an R-matrix defined in a region, $i-1$ to region i. Assuming that there is the global R-matrix through region $i-1$

$$\mathbf{u}(r_{i-1}) = \mathbf{R}_{i-1}\dot{\mathbf{u}}(r_{i-1}) \quad (35)$$

relates the radial function $\mathbf{u}(r_{i-1})$ and its derivatives, $\dot{\mathbf{u}}(r_{i-1})$, at the rightmost boundary, where we use a boldface notation to mean vectors and matrices in the channel indices. In the ith region, one can relate the values of the functions to their derivatives via

$$\mathbf{u}(l_i) = \mathbf{r}_i(l_i|r_i)\dot{\mathbf{u}}(r_i) - \mathbf{r}_i(l_i|l_i)\dot{\mathbf{u}}(l_i) \quad (36)$$

$$\mathbf{u}(r_i) = \mathbf{r}_i(r_i|r_i)\dot{\mathbf{u}}(r_i) - \mathbf{r}_i(r_i|l_i)\dot{\mathbf{u}}(l_i) \quad (37)$$

where r_i are the sector R-matrices for region i. Using equations 35–37 and the fact that the functions (derivatives) on the left in region i are equal to those on the right in region $i-1$ yields an expression for the new global R-matrix

$$\mathbf{R}_i = \mathbf{r}_i(r_i|r_i) - \mathbf{r}_i(r_i|l_i)[\mathbf{R}_{i-1} + \mathbf{r}_i(l_i|l_i)]^{-1}\mathbf{r}_i(r_i|r_r) \quad (38)$$

One may use any approach to compute the sector R-matrices, including expanding in a basis. One popular technique is to make the sectors small enough that the potential can be taken to be a constant within that sector. This allows a construction of the sector R-matrices as trigonometric functions after diagonalizing the constant coupling matrix.

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used basis sets with a fixed boundary condition on the R-matrix surface[83,84]. Later work showed how to relax the fixed boundary condition and extend the method to molecular targets[85–93] (for in-depth reviews, see REFS[94–96]). A more exact treatment of scattering phenomena from heavier atoms and molecules often requires inclusion of relativistic effects. For relativistic treatments, we recommend the reviews in REFS[97–100].

To generalize the relevant equations to molecules the inter-nuclear distances $\mathbf{R}$ should be included in the notation. Within the Born–Oppenheimer approximation, the Schrödinger equation inside the R-matrix radius may be written as

$$[H_{N+1}(\mathbf{r};\mathbf{R}) + L_{N+1} - E(\mathbf{R})]|\Psi(\mathbf{r};\mathbf{R})\rangle$$
$$= L_{N+1}|\Psi(\mathbf{r};\mathbf{R})\rangle \tag{7a}$$

$$L_{N+1} = \sum_{i=1}^{N+1} |\psi_c\rangle \frac{1}{2}\delta(r_i - a)\left(\frac{\partial}{\partial r_i} - b\right)\langle\psi_c| \tag{7b}$$

Here, H_{N+1} is the $N+1$ electron Hamiltonian, E is the energy and L_{N+1} is the Bloch operator[101] that has been added and subtracted to the Schrödinger equation to ensure a well-defined boundary condition on the R-matrix surface ($r = a$). The parameter b may be chosen to be any real number. To solve this equation, we expand the wavefunction in a basis set

$$|\Psi_k\rangle = \sum_{c=1}^{N}\sum_{i=1}^{m} a_{ci,k}|\psi_c u_{ci}^0\rangle + \sum_{q=1}^{M} b_q|\chi_q\rangle \tag{8}$$

which satisfies the following eigenvalue problem

$$[H_{N+1}(r;R) + L_{N+1} - E_k(R)]|\Psi_k\rangle = 0 \tag{9}$$

Here, χ_q are a set of $(N+1)$ electron correlation functions, m refers to the number of u_{ci}^0 functions and u_{ci}^0 are a suitable set of radial functions to expand the scattering function. The u_{ci}^0 are often chosen to satisfy a set of simpler model scattering equations. The use of a real number b in the Bloch operator, L_{N+1}, provides a convenient approach to ensure that the R-matrix eigenstate energies are real. In the original formulation of the R-matrix method, the eigenstates were chosen to have a fixed and zero derivative ($b = 0$) on the bounding surface. When a complete set of u_{ci}^0 are used, the boundary condition is unimportant, but if one uses a restricted set of functions, convergence can be quite slow. An approximate correction, first suggested in REF[102], was used to ameliorate the problem.

By expanding the solutions to equation 7a in terms of the solutions to equation 9 and then projecting onto the target states, ψ_c and setting $r = a$, one obtains

$$u_c(a) = \langle\psi_c\delta(r_{N+1} - a)|\Psi\rangle$$
$$= \sum_{d=1}^{n} \mathscr{R}_{c,d}\left[\frac{\partial u_d(r)}{\partial r} - bu_d(r)\right]_{r=a} \tag{10a}$$

$$\mathscr{R}_{c,d} = \frac{1}{2}\sum_{k} \frac{u_{ck}(a)u_{dk}(a)}{[E_k(R) - E(R)]} \tag{10b}$$

$$u_c(a) = \sum_{i} a_{ci,k}u_{ci}^0(a) \tag{10c}$$

In numerical applications, the use of the Bloch operator has important practical consequences. As mentioned earlier, if a basis is chosen satisfying fixed boundary conditions on the R-matrix surface, convergence to the scattering solution is typically quite slow since the true scattering function does not satisfy those boundary conditions. Corrections[102] can be made to help alleviate the slow convergence but by using the Bloch operator, it is possible to use an expansion basis u_{ci}^0 in equation 10c having arbitrary boundary conditions on the R-matrix surface. This substantially improves convergence and more importantly, widens the selection of possible basis sets for numerical calculations.

For example, in electron scattering from molecular targets, it is convenient to use multicentre functions such as Gaussians as a basis and such expansions are possible within the Bloch-operator formalism. In using Gaussians, it has been found that it is necessary to use formulas for the integrals that remove the contributions between $r = a$ and $r = \infty$ for diffuse Gaussians that are needed to represent the scattering orbitals[93]. This procedure is straightforward since for most of these integrals multipole expansions are sufficient. For atomic R-matrix calculations, numerical, B-spline and FE orbitals have been successfully used[103,104].

The R-matrix method may be generalized to include the effects of nuclear excitation and even dissociation. The interested reader should consult REF[92] for details.

It is possible to choose b in an arbitrary manner. Specific choices of b enable us to recover many of the formal approaches to the collision problem such as the Kapur–Peierls or Siegert expansions[81,105,106].

To obtain the final solution to equation 10a, its is necessary to match $u_c(a)$ to appropriate asymptotic forms at the boundary surface $r = a$. If one can find appropriate matching functions for the solutions between $r = a$ and where the potential has vanished, the process is straightforward. Since exchange is absent in the region beyond the R-matrix surface, the coupled differential equations may be integrated inward or combined with asymptotic expansions to produce the solutions required for the matching.

A more elegant approach is to devise a method that would propagate the R-matrix from the surface to very large distances where matching to free waves would be sufficient. A number of R-matrix propagation techniques exist to accomplish just that[107–109]. The idea is basically to apply the R-matrix for a series of subregions from $r = a$ to where the potential may be neglected. In each of these subregions, or sectors, approximations are made to the potential which enable the sector R-matrices to be easily computed and by recursion relations produce the R-matrix on the larger region. Such methods are typically stable even in the presence of closed channels.

Note that when there are very large numbers of channels in the outer region, the solution of these equations can become expensive as they need to be repeated at each scattering energy.

One criticism of the R-matrix method is that it introduces an artificial boundary that in reality does not exist. Although this may be unappealing conceptually, in practice the consequences are minor as long as the matrix elements inside a fixed radius can be computed. A more serious issue is the need to obtain all of the eigenvalues and eigenvectors of what can be an extremely large matrix. Even though there are techniques available to do this using distributed memory computers, this can be costly. There are two methods available to avoid the calculation of all eigenpairs. The first approach is exact: compute the Green's function or resolvent by solving a set of linear algebraic equations[50]. The second approach is to find a reliable approximation to perform the sum over the higher-lying energies of the Green's function. The first approach loses the advantage of needing only a single major computational step to obtain the scattering information at all energies. There are ways to make this more efficient that have not been explored. For example, using an iterative approach to the solution of the linear equations based on a previous direct solution to a model problem as a preconditioner[110] could be effective and has been shown to work in other contexts. The second approach, to find an approximate technique to include the higher-lying R-matrix energies, has been explored in REFS[111,112]. Although the second approach has been shown to work in a number of cases by testing against an exact solution, one clearly needs to be careful in trusting that it does work in practice.

Finally, we should mention the connection of the R-matrix method to quantum defect theory[113]. In the present context, quantum defect theory explores the behaviour of quantities such as the reaction matrix, as a function of the energy above and below the scattering threshold. This enables the understanding of how certain analytic functions of the energy behave when going from an energetically closed to an energetically open state[114]. Stated in a simpler way, the quantum defects used to describe the energetics of high-lying Rydberg states may be extrapolated above threshold to compute scattering phase shifts. Since the R- and K-matrices are related, it is an algebraic exercise to connect the two theoretical formulations.

R-matrix theory applications. Applications of R-matrix theory to atomic and molecular scattering abound. In this section, we restrict ourselves to works published in the past decade, those that have appeared subsequent to the three major R-matrix review articles published earlier[94–96]. On the molecular front, theoretical studies have been conducted on photoionization of NO (REF.[115]), NO_2 (REFS[116,117]), N_2 (REFS[118,119]), methane[119], endohedral fullerenes Xe@C_{60} (REF.[120]) and CO_2 (REF.[121]). Electron scattering from N_2 and CO_2 are the best known systems and show good agreement with experimental results and calculations performed by multiple groups[119,121,122].

For atomic targets, the Belfast R-matrix codes, whose development began in the 1970s, are being used worldwide to study atoms and ions of astrophysical interest and of importance to fusion. There are also numerous theoretical studies and experimental comparisons using the more recently developed B-spline R-matrix (BSR-matrix) code[123], to a number of interesting systems. This code uses a set of non-orthogonal orbitals for the bound and continuum orbitals and a set of B-splines that define the R-matrix basis functions. It also adds relativistic effects by adding the Breit–Pauli Hamiltonian[124] as a first-order correction. Recent calculations using this code include the electron-impact excitation of Zn (REF.[125]), the single and double photoionization of Ne (REF.[126]), electron-impact excitation and ionization of atomic Ca (REF.[127]).

The R-matrix method has been generalized to include time-dependent interactions (RMT). Using various short-time propagators in the inner region and a FD grid representation of the single-electron wavefunction in the outer region, it is possible to account for the interaction of the electrons with time-varying electromagnetic fields[128–130]. RMT has also been applied to double photoionization of He (REF.[129]) and photodetachment of F^- in strong, circularly polarized laser fields[131,132].

Fully relativistic versions of R-matrix codes exist and are used in applications with highly charged ions and heavy atoms, for example, in studies on electron-impact excitation and ionization of W^{3+}, N IV (REF.[133]) and Fe II (REFS[134,135]).

Kohn variational method. Walter Kohn developed a variational method[36] to treat collision problems as part of his doctoral thesis research with Julian Schwinger. The method, now known as the Kohn variational method, has been widely applied to collision problems in nuclear, atomic and molecular physics[40,136].

As in the R-matrix method, the wavefunction is expanded in a basis set, but the basis is required to satisfy the known asymptotic boundary conditions. The matching at some known radius, as in the R-matrix method, is replaced by computing the free-free and bound-free matrix elements of the Hamiltonian. Such matrix elements can often be complex to evaluate because the free basis functions have an oscillatory behaviour. The wavefunction is then expanded as the known incident wave plus a linear set of trial functions with unknown coefficients. The variational conditions are then used to reduce the scattering problem to a set of linear algebraic equations. As the colliding particles move to larger separations, at least one of the unknown coefficients contains the desired scattering information.

The variational principle may be applied to the S-, T- and K-matrices, depending on the boundary conditions imposed on the wavefunction. These matrices are all mathematically related and each provides information on the scattering amplitudes of the collision problem. The variational principle provides a method to expresses a variationally corrected S-, T- or K-matrix element in terms of a trial value obtained by solving a set of linear equations. The linear equations in turn are obtained by a variation of the coefficients in the expansion of the trial solution[137–143].

Quantum defect
In this context, it refers to an expression for the energy of a Rydberg state in an atom that replaces the hydrogenic integer quantum number *n*, by a non-integer value. The deviation from the integer is called the quantum defect. The correction accounts for the fact that the inner electrons partially screen the bare nuclear charge.

S-, T- and K-matrices
These are a family of scattering matrices that relate the initial states in a scattering process to the possible final states. All three matrices are related to each other mathematically. The S-matrix expresses the states in terms of exponential free waves, whereas the K-matrix expresses the states in terms of sine and cosine functions. The T-matrix uses a mixture of exponential and trigonometric functions.

To illustrate the method, consider the *s*-wave radial scattering problem

$$\hat{L}\psi(r) = [\hat{H}_0 + V(r) - E]\psi(r)$$
$$= \left[-\frac{1}{2}\frac{d^2}{dr^2} + V(r) - E\right]\psi(r) = 0$$

Here H_0 is the kinetic energy term and $V(r)$ a local potential. The boundary conditions on $\psi(r)$ are

$$\psi(0) = 0 \qquad (11)$$

$$\lim_{r\to\infty}\psi(r) = f(r) + \lambda g(r) \qquad (12)$$

where $f(r)$ and $g(r)$ are two, linearly independent solutions to the radial Schrödinger equation of $\hat{H}_0$. The choice of the linearly dependent pairs determines whether we are looking for $\lambda =$ S-, T- or K-matrix elements. The KVP for the K-matrix has some unpleasant aspects. Since one has to invert a real, symmetric matrix, it is possible for mathematical singularities to occur. These make the expressions undefined at certain energies. Although there are workarounds, it seems better to avoid the problem from the outset by using the KVP for the T- or S-matrices, which do not suffer from this problem. The price paid is that one is required to deal with a set of complex algebraic equations.

The variational principle is illustrated here using potential scattering in one dimension[140]. Given the functional

$$L = \langle\psi|\hat{L}|\psi\rangle \equiv 0 \qquad (13)$$

its variation is examined by

$$\delta L = \langle\delta\psi|\hat{L}|\psi\rangle + \langle\psi|\hat{L}|\delta\psi\rangle + \langle\delta\psi|\hat{L}|\delta\psi\rangle \qquad (14)$$

The third term is neglected to first-order accuracy. The first term is zero. If $\delta\psi = \psi - \psi^t$ where ψ^t is an approximate trial solution satisfying the same boundary conditions as equations 11 and 12, the second term is equivalent to $-\langle\psi|\hat{L}|\psi^t\rangle$. Integrating in space by parts twice, and using the fact that ψ is the exact solution to the differential equation, yields[144]

$$\langle\psi|\hat{L}|\delta\psi\rangle = -\langle\psi|\hat{L}|\psi^t\rangle = -\frac{\delta\lambda W}{2} \qquad (15)$$

where

$$W = \det\begin{pmatrix} f(r) & g(r) \\ df(r)/dr & dg(r)/dr \end{pmatrix} \qquad (16)$$

is the Wronskian. Therefore

$$\delta\left[L + \frac{\lambda W}{2}\right] = 0 \qquad (17)$$

and from here one obtains the Kato identity[140,145]

$$\lambda^S = \lambda^t + \frac{2}{W}\langle\psi^t|\hat{L}|\psi^t\rangle \qquad (18)$$

In Kohn's variational method, equation 18 is solved by using $N+1$ trial functions $[g(r), \phi_i(r)]$ with linear trial coefficients

$$\psi^t(r) = f(r) + \lambda^t g(r) + \sum_{i=1}^{N} c_i \phi_i(r) \qquad (19)$$

where $\phi_i(r)$ are a set of $\mathscr{L}^2$ functions.

Substituting the solution of equation 19 into the Kato identity and projecting onto $\langle g|$ and then $\langle\phi_i|$ leads to a set of linear equations. Using the symbol, 0 for f, 1 for g and b for the set $\langle\phi_i|$, these matrix equations become

$$\mathbf{m}_{00} = \hat{L}_{00} - \hat{L}_{0b}\hat{L}_{bb}^{-1}\hat{L}_{b0} \qquad (20a)$$

$$\mathbf{m}_{11} = \hat{L}_{11} - \hat{L}_{1b}\hat{L}_{bb}^{-1}\hat{L}_{b1} \qquad (20b)$$

$$\mathbf{m}_{10} = \hat{L}_{10} - \hat{L}_{1b}\hat{L}_{bb}^{-1}\hat{L}_{b0} \qquad (20c)$$

This formalism incorporates the bound-state subspace into the continuum subspace using partitioning. Substituting equation 19 into equation 18 and using equations 20a–20c plus

$$\mathbf{m}_{10}^\dagger = \frac{1}{2}W + \mathbf{m}_{01} \qquad (21)$$

yields a very compact expression for the variationally corrected quantity

$$\lambda = \frac{2}{W}[\mathbf{m}_{00} - \mathbf{m}_{01}^\dagger\mathbf{m}_{11}^{-1}\mathbf{m}_{10}] \qquad (22)$$

The generalization to the full multichannel problem is straightforward. The trial function is

$$\Psi^c = \sum_{c'}\mathscr{A}\left[\psi_c F_{c'}^c\right] + \sum_i d_i \chi_i \qquad (23)$$

where $\psi_{c'}$ are a set of N-particle target states, $F_{c'}^c$ a single-particle function that describes the scattered particle and χ_i a set of $(N+1)$-particle antisymmetric $\mathscr{L}^2$ states. The operator $\mathscr{A}$ antisymmetrizes $F_{c'}^c$ and $\psi_{c'}$. The channel continuum functions $F_{c'}^c$ can be further expanded in terms of spherical harmonics and radial functions akin to those in equation 12 that are linearly independent continuum orbitals and are regular at the origin. The generalization of the variational principle to the multichannel case is

$$\lambda_{c,c'}^S = \lambda_{c,c'}^t + \frac{2}{W}\langle\Psi^c|\hat{L}|\Psi^{c'}\rangle \qquad (24)$$

There are some important practical numerical issues associated with solving these equations (BOX 4).

Box 4 | **Kohn method practical numerical issues**

In the full multichannel problem, it is computationally convenient to work with an orthonormal $(N+1)$-particle basis. The channel orbitals $F_{c'}^c$ in equation 23 are expanded as linear combinations of bound and free (that is, continuum) states

$$F_{c'}^c = f_{c'}\delta_{cc'} + \lambda_{cc'}^t g_{c'} + \sum_i \alpha_i^{c'} \phi_i^{c'} \qquad (39)$$

where $f_{c'}$ and $g_{c'}$ are the free orbitals, $\phi_i^{c'}$ are the bound functions, and α, λ and δ are variational coefficients. The continuum functions $f_{c'}$ and $g_{c'}$ are orthogonalized to all the $\mathcal{L}^2$ functions appearing in equation 39. This has the effect of imposing a strong orthogonality condition between the Θ_c target states and the newly orthogonalized channel functions.

The $\{\Theta_c \phi_i^c\}$ functions that appear in equation 23 are divided into two categories: functions where the N-particle part Θ_c contains one or more determinants containing the added ϕ_i^c orbital and those that do not contain such terms. The first category functions are required to relax the strong orthogonality constraint that is imposed on the channel wavefunction and are limited in number. These terms are most easily treated by moving them into the second term of equation 23. This procedure separates the wavefunction into a $P\Psi^c$ and $Q\Psi^c$ part using the terminology of Feshbach resonances[167,168]. In contrast to the single channel case, the P-space part of the multichannel wavefunction now contains an $\mathcal{L}^2$ part (that is the second category $\{\Theta_c \phi_i^c\}$ functions).

As an example, consider the ^2S symmetry of a hydrogen atom. The appropriate term to include in Q-space in this case is the $|1s^2$ term[51]. Other terms that belong to Q-space in this example are terms of the form $|\phi_i \phi_j\rangle$ where i runs overall indices except $1s$. What remains in the P-space are then terms of the form $|1s\phi_i\rangle$ where ϕ_i is not $1s$.

The Q-space part may be formally replaced by an optical potential which results in an effective Hamiltonian

$$\mathbf{H}_{eff} = \mathbf{L}_{PP} + \mathbf{L}_{PQ}\mathbf{L}_{QQ}^{-1}\mathbf{L}_{QP} = \mathbf{H}_{PP} - \mathbf{V}_{opt}$$

operating only on the P-space part of the wavefunction. Here $\mathbf{L}_{QQ}^{-1}$ is the inverse of the Hamiltonian matrix spanned by the χ_i functions and $\mathbf{V}_{opt}$ is the optical potential.

The multichannel form of equation 22 is[40,140]

$$\lambda^S = \frac{2}{W}\left[\mathbf{M}_{oo} - \mathbf{M}_{oq}^\dagger \mathbf{M}_{qq}^{-1} \mathbf{M}_{qo}\right] \qquad (40)$$

Here index o refers to the space spanned by $\{\Theta_c f_c\}$, and q the space spanned by $\{\Theta_c g_c\}$ and $\{\Theta_{c'}\phi_i^{c'}\}$.

At this point, the required theoretical developments are in hand and all that is needed is to construct the Hamiltonian matrix elements. For atomic systems, this has already been done. For molecules, it is possible to construct all the direct terms in the Hamiltonian matrix elements by a mixture of analytic and straightforward numerical techniques. This is not the case for the exchange and optical potential terms. There is a mathematical approximation, which is physically motivated, to eliminate these terms. It is based on the assumption that once the set of bound-state orbitals is sufficiently large, the orthogonalization process removes all of the amplitude of the channel function inside the molecular region where exchange and correlation are important. Under these conditions, the exchange and optical potential matrix elements are

$$M^{ex} \approx \sum_{ij}\langle \mathcal{A}(\Theta_c f_c)|\phi_i\rangle M_{ij} \langle\phi_j|\mathcal{A}(\Theta_{c'}f_{c'})\rangle = 0 \qquad (41)$$

and can therefore be neglected. The advantage of the approximation is that no free-free or bound-free matrix elements involving exchange of the optical potential interactions survives. The exchange effect is instead incorporated into the bound-bound components of H_{eff}, which are readily computed with electronic structure codes.

Kohn variational method applications. Applications of the Kohn variational method to electron–atom collisions, seem to have diminished after the 1990s. In contrast, when it comes to electron–molecule collisions and photoionization, the opposite is true. Here we outline a few of the recent applications of the method over the past decade.

An interesting example is the use of the complex Kohn and polyatomic Schwinger variational techniques to study interchannel coupling correlation effects in the valence photoionization dynamics of SF_6 with good agreement between the two calculations and the experimental results[146]. This study revealed the importance of interchannel correlations and determined a long-debated ordering of the valence orbitals of the compound. Other applications to molecules are calculations of excitation of water by a low-energy electron impact[147], experimental and theoretical investigations of the dynamics of dissociative electron attachment to methane[148], hole localization in K-shell and core-valence-excited acetylene photoionization[149], and photo-electron angular distributions for core ionization of ethane, carbon tetrafluoride and 1,1-difluoroethylene[150], to name a few.

The complex Kohn variational method was also used to compute light-driven electronic transitions between continuum wavefunctions in atomic and molecular systems. This development enabled the study of multi-photon processes in the perturbative regime for arbitrary light polarization. The method was applied to compute the photoelectron spectrum arising from a pump–probe, two-photon ionization of helium experiment induced by a sequence of extreme utraviolet and infrared-light pulses[151].

A final example involves computational studies of positronium (Ps) scattering off of hydrogen. This is a very difficult problem that has been used as a test case for comparing scattering approximation methods. The Kohn variational method has often been considered as the gold standard for this problem. Recent comparisons between the R-matrix method for the *s*-wave scattering in Ps–H collisions has shown that the phase-shift calculations done with both methods agree to within less than 4%[152]. In REF.[153], a study was conducted on Ps–H, e⁻–H and e⁺–H scattering using various versions of the Kohn variational method. The calculations revealed qualitative agreement of the integrated cross-sections for the first two processes, but for the same process there was significant disagreement between the partial wave cross-sections at low energies.

Comparisons of the methods

If we look at the case of scattering of electrons from atoms as an example, where comparisons are possible, both the CCC- and BSR-matrix methods are quite competitive and also quite accurate. By quite accurate, we mean that they reproduce the results of well-designed experiments. In fact, in some instances, where discrepancies exist, the calculations have been found to be more accurate than experiment as shown by performing the experiments again more carefully or with improved experimental techniques[123]. The CCC approach has some advantages for quasi two-electron systems because the codes have been written to explicitly cover these systems. The Belfast and BSR-matrix codes are fully general codes[94,103], capable of treating atomic systems with any number of electrons. This places certain practical restrictions on the size of the state expansions that are computationally tractable. But here too, there have been

cases where the calculations have pointed to experimental errors which, when corrected, agree quite well with each other.

The Kohn variational method saw a number of successful applications to atomic systems when it was introduced in the late 1960s–1980. For some reason, it was not pursued as vigorously as the R-matrix and CCC approaches, which still dominate the field today. Perhaps this was a consequence of the anomalous singularities present in the K-matrix version of the method, which require special attention, but it was more likely due to the persistence of a number of groups working diligently to write the computer codes needed to apply the methods to realistic problems. As an aside, there is no reason why the complex versions of the Kohn variational method cannot have singularities, but it has been shown[154] that these are a consequence of using an incomplete basis set and rarely occur in practice.

The situation for molecules is different. Calculations of electron–molecule collisions have been dominated by the R-matrix method[95] and the complex Kohn variational method[136]. The former grew out of the Belfast atomic R-matrix codes[155], which were preceded by earlier efforts[156]. The early complex Kohn work was initiated at Los Alamos National Laboratory[138,141] and many of the subsequent and important developments came from the Lawrence Berkeley Laboratory/UC Davis group[140].

The molecular collisions problem, especially for general polyatomic molecules, is difficult computationally and subject to limitations in the size of the wavefunction expansion that can be used. Nonetheless, both the R-matrix and Kohn variational method have been quite successful in describing a number of processes of interest in both electron scattering and photoionization of small- to medium-sized molecular systems. Where comparisons between the two approaches are available, they often do not agree quantitatively and in some instances show qualitative differences.

Time-dependent problems

Although reformulating the time-independent collision problem as a time-dependent problem using wavepackets can be useful, the focus of this Technical Review is on problems with a truly time-dependent interaction such as an atom or molecule exposed to an intense, short-pulse, time-varying, laser field. The target, exposed to this external perturbation may undergo excitation and/or ionization. If the radiation can ionize the target, the continuous spectrum must be treated and many of the approaches used in time-independent collision theory remain formally and often computationally relevant.

However, the mathematical difference is that a time-dependent problem is an initial value problem not a boundary value problem, which requires that the solution be propagated in time from some starting value, t_0, to some final value, t_f where the physically relevant quantities are extracted. In some cases, this last step can be the most difficult to formulate in a computationally tractable fashion. In most physically interesting problems, the laser field is on for some finite period and then turned off. The system then propagates in the

Hamiltonian of the field-free system and after some suitable time, the wavefunction is interrogated for the probability of being in some final state of the field-free system. Clearly, during this final phase, the methods used for the time-independent problem are relevant, but even when the system is exposed to laser radiation, expansions such as those described in the previous section are useful. Of course, the coefficients of the terms in that expansion are time dependent. Consequently, it is not surprising that many of the methods developed for collision problems are also useful in the time-dependent case.

When ionization becomes a factor in describing the interaction of radiation with an atom or molecule, the stationary-state wavefunctions for the continuum in the absence of the field can be used as a basis for the time-dependent problem. They also can be useful in reducing the computational effort in computing various probabilities when the field is turned off.

The essential difference is that it is necessary to propagate the wavefunction in a time-dependent potential while the field is on. There are a variety of methods to accomplish this. Some only require knowledge of the wavefunction at the previous time steps, others make some use of future information. In the former instance, there are both explicit and implicit approaches. Implicit methods typically require the solution of a set of algebraic equations at the previous and current time. In this Technical Review, we concentrate on methods that approximate the exact propagator

$$\hat{U}(t;t_0) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots$$
$$\int_{t_0}^{t_{n-1}} dt_n T[\mathbf{H}(t_1)\mathbf{H}(t_2) \cdots \mathbf{H}(t_n)]$$

(25)

where T is the time ordering operator. Here $U(t;t_0)$ is the propagator that takes a system from time t_0 to t and $(H(t_i))$ is the Hamiltonian of the system at time t_i. For short times (δt), the time ordering operator may be neglected and one obtains

$$\hat{U}(t_0 + \delta t; t_0) \approx \int_{t_0}^{(t_0+\delta t)} \exp - i[\mathbf{H}(t)t] \, dt$$

(26)

This approximation can lead to error accumulation in the phase and convergence. Therefore, the size of the time step should be treated carefully to monitor the accuracy. There are other more computationally expensive methods that could avoid this approximation[157]. If the integral is approximated using the midpoint rule, one obtains

$$\hat{U}(t_0 + \delta t; t_0) \approx \exp\left(-i\left[\mathbf{H}\left(t_0 + \frac{\delta t}{2}\right)\right]\delta t\right)$$

(27)

The application of this exponential to the wavefunction at t_0 is the major computational process. Since $\mathbf{H}(t)$ is, in principle, a large matrix, if one could easily and efficiently diagonalize $\mathbf{H}(t)$, the eigenvalues and eigenvectors could be used to evaluate the exponential. In general, this would be a very computational expensive

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Padé approximate
A numerical method that approximates a function by a rational function of two polynomials.

Coupled cluster
This is a numerical quantum chemical method used for describing many-body systems. Coupled cluster takes an assumed reference basic configuration (such as the Hartree–Fock wavefunction) and constructs multi-electron wavefunctions using an exponential operator ansatz to add electron correlation. The cluster expansion must be truncated in practice due to the complexity of the resulting nonlinear equations.

Box 5 | Lanczos iteration

The Lanczos iteration method was initially developed to find the smallest and largest eigenpairs of a large, sparse, $n \times n$ symmetric matrix[159,169,170]. The method requires the application of an often large, but sparse matrix to a vector. Specific routines that exploit the structure of the matrix can be developed to perform that operation efficiently.

In effect, the Lanczos method may be viewed as reducing the large, $\mathbf{H}_{n \times n}$ matrix to a (hopefully) smaller, $\mathbf{H}^{(\Lambda)}_{m \times m}$ tridiagonal matrix, where ideally $m << n$ of the eigenpairs of interest may be computed accurately. If the iteration continues until $m = n$, the eigenvalues and eigenvectors of $\mathbf{H}^{(\Lambda)}$ would be identical to those of the $\mathbf{H}_{n \times n}$. A naive implementation of the Lanczos iteration can lead to linear dependence which has a number of undesired side effects[110,170,171]. To circumvent linear dependence often requires additional and expensive re-orthogonalization procedures.

The transformation between the two representations is given by:

$$\mathbf{H}^{(\Lambda)} = \mathbf{Q}^T \mathbf{H} \mathbf{Q} \tag{42}$$

where $\mathbf{Q}_{n \times m} = [|q_1\rangle |q_2\rangle \ldots |q_m\rangle]$ are the Lanczos vectors at the mth step of the process. One can view these vectors as linear combinations of the so-called Krylov subspace vectors

$$K(H, q, m) = \mathrm{span}\{|q_1\rangle, \mathbf{H}|q_1\rangle, \mathbf{H}^2|q_2\rangle, \ldots, \mathbf{H}^{m-1}|q_1\rangle\} = \mathrm{span}\{|q_1\rangle, |q_2\rangle, |q_3\rangle, \ldots, |q_m\rangle\}$$

where

$$\beta_{k+1}|q_{k+1}\rangle = (\mathbf{H} - \alpha_k \mathbf{I})|q_k\rangle - \beta_{k-1}|q_{k-1}\rangle \tag{43}$$

The vectors in equation 43 form an orthonormal set. The recursion relation may be started with any vector and continued until the desired eigenvalues are found to sufficient accuracy.

The application of the Lanczos method to time propagation is not directly related to the question of determining the eigenvalues[157,172–174]. The process may be stated as follows: let the first Lanczos vector, $|q_1\rangle = |\psi(x, t)\rangle$. How can one determine a small set of additional vectors, $|q_2\rangle \ldots |q_m\rangle$, which effectively span the new subspace defined by $|\psi(x, t + \delta t)\rangle$ and provide a representation of the exponential function over the time step? Assuming that the time step is small enough that one can approximate the interaction of the electrons with the field by using the field's value at the midpoint of the time step, then the time evolution operator, U, may be approximated as

$$\hat{\mathbf{U}}(t + \delta t | t) = \exp\left[-i\hat{\mathbf{H}}\left(x, t + \frac{\delta t}{2}\right)\delta t\right] \tag{44}$$

The size of the Krylov subspace matrix, $\mathbf{Q}$, is a function of the accuracy demanded and the size of the time step. The tridiagonal matrix

$$\mathbf{H}^{(\Lambda)} = \begin{bmatrix} \alpha_1 & \beta_2 & & & \\ \beta_2 & \alpha_2 & & & \\ & & \ddots & & \\ & & & \alpha_{m-1} & \beta_m \\ & & & \beta_m & \alpha_m \end{bmatrix} \tag{45}$$

may be easily diagonalized for the eigenpairs and the wavefunction at the next time step computed as

$$|\Psi(x, t + \delta t)\rangle = \sum_i |\lambda_i\rangle \exp(-i\lambda_i \delta t)\langle \lambda_i | \Psi(x, t)\rangle \tag{46}$$

approach even if the diagonalization was possible. Since one really only requires the action of the exponential on a known vector, other methods are more effective. One such approach, called the Crank–Nicholson method[158], approximates the exponential as a Padé approximate

$$\hat{\mathbf{U}}(t_0 + \delta t ; t_0) \approx \frac{I - i\frac{\delta t}{2}\mathbf{H}\left(t_0 + \frac{\delta t}{2}\right)}{I + \frac{\delta t}{2}\mathbf{H}\left(t_0 + \frac{\delta t}{2}\right)} \tag{28}$$

(where I is the identity matrix), which leads to the following set of linear equations

$$\left[I - i\frac{\delta t}{2}\mathbf{H}\left(t_0 + \frac{\delta t}{2}\right)\right]\Psi(t_0 + \delta t) = \left[I + i\frac{\delta t}{2}\mathbf{H}(t_0 + \frac{\delta t}{2})\right]\Psi(t_0) \tag{29}$$

In practice, the composite exponential is 'split' into simpler parts and the Padé approximation applied to the separate parts to make the linear equations easier to solve. These manipulations all preserve the second-order accuracy of the method.

Another quite effective approach to computing the exponential is the short iterative Lanczos method[159] (BOX 5). The basic idea is to use a vector space constructed from the repetitive application of the Hamiltonian to a vector to perform an 'effective' diagonalization of the Hamiltonian.

The takeaway message is that in all of these techniques, the action of the Hamiltonian on a vector is required and some basis is needed to perform that operation. For this basic operation, a discretization of the Hamiltonian is required. Stated differently, some spatial basis is required to perform the needed operation. Often, it is the bound and continuum states of the unperturbed system that are the most convenient or accurate way to perform that operation. They certainly reduce the efforts needed to extract accurate transition probabilities once the field is turned off. That said, it is often neither practical nor convenient to use the basis of the unperturbed system to expand the time-dependent wavefunction while the electromagnetic field is on. When the radiation cannot ionize the target, the easiest procedure is to expand in some computationally convenient $\mathscr{L}^2$ basis with time-dependent coefficients and reduce the problem to a set of coupled, time-dependent algebraic equations that are solved using one of the techniques discussed earlier. When the electromagnetic field is such that the system can be ionized, the most logical and convenient approach is to generalize the CC expansion to have time-dependent coefficients[160]. So, once again, the treatments developed for the collision problem come into play. The inevitable conclusion is that all of the efforts of previous decades are essential to solving today's problems.

We conclude this section by mentioning that there are numerous newer developments in the treatment of the time-dependent Schrödinger equation relevant to strong-field laser processes. These include multi-configuration time-dependent Hartree–Fock approaches[161] and the orbital adaptive time-dependent coupled cluster method[162], where variational principles are applied to a N-body wavefunction ansatz; configuration interaction methods with single excitation[163], which is effectively a one-electron theory with coupled channels; complete-active-space self-consistent-field

methods[164], where both the configuration interaction coefficients and the shape of the orbitals are variationally optimized; time-dependent R-matrix methods[130,165], using the usual division of space into two regions; an inner region where the interaction of the electron and the laser is included and an outer region where a one- or two-electron scattering problem is solved on a finite-difference grid.

Published online 16 December 2019

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