

# Numerical methods every atomic and molecular theorist should know

B. I. Schneider\*<sup>1</sup> and H. Gharibnejad<sup>1</sup>

<sup>1</sup>Applied and Computational Mathematics Division, Information Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8910

\*e-mail: barry.schneider@nist.gov

## 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.

## [H1] Introduction

Our ability to compute the ground 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 modeling 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.

## [H2] Early history

### [H3] Atomic and molecular structure

Most of computational AMO physics has its roots in developments which 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<sup>1,2</sup>, John Clarke Slater<sup>3</sup>, Vladimir Fock<sup>4</sup> and others (see Ref.<sup>5</sup> for a historical perspective.) Its extension to include exchange effects, as in the Hartree-Fock equations, were first solved for atoms using numerical techniques developed to approximate differential equations by difference equations on an analog computer called the differential analyzer<sup>6</sup>. 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 laborious, 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<sup>7</sup> and George G. Hall<sup>8</sup>. With 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.<sup>9-13</sup>

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<sup>14–19</sup> were pursuing an alternative numerical treatment of He and H<sub>2</sub>. They abandoned 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<sub>2</sub>. 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.<sup>20–24</sup>

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 which may then be superposed using the variational principle to get the optimal energy. This approach, termed configuration interaction (for very early applications, see Refs<sup>25,26</sup> and for a historical overview Ref.<sup>27</sup>) remains today<sup>28,29</sup> one of 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.

### **[H3] Atomic collisions**

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

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.<sup>34–39</sup> Variational principles were eventually developed applicable to both electron and heavy particle collision problems. Variants of these methods are still in use today (See Ref.<sup>40</sup> for a thorough discussion.)

### **[H2] 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 modeling of astrophysical, fusion and lighting plasmas. Experiments cannot supply the data needed for this modeling 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 of 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 time scales comparable to the motion of the electrons in these systems and even to manipulate them to control the outcome of chemical reactions.<sup>41,42</sup> In this case, the problem is actually time-dependent, a further complexity, but in order 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 time scale 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.

## [H1] 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<sup>43</sup> (FD), a basis set expansion<sup>44</sup> (spectral) or the use of numerical quadrature<sup>45</sup>. 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. A serious use of integral equations began in the 1970s (see Refs<sup>46-53</sup>) and variants of the original methodology still exist. Basis set expansions may be defined globally or over a set of sub-domains (finite-elements, or FE)<sup>54-59</sup> which 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 finite-difference 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.<sup>60-64</sup>

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<sup>50</sup> where the finite differences 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 (PDE) are reduced to a set of algebraic equations<sup>50,65,66</sup>. In the time-dependent case, the PDEs 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 article, 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.

## [H1] 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 method (CC)<sup>67-70</sup>, uses an expansion of the collision wavefunction  $\Psi$  of the form,

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

where  $\psi_c$  is a state of the  $N$  electron target atom and  $F_c$ , the unknown channel function that is antisymmetrized into  $\psi_c$  as indicated by the  $\mathcal{A}$  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  $\psi_c$  and integrating over the target coordinates, leads to a set of coupled, integro-differential equations of the general form,

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

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.

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.

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

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

The  $b_q$  are variational parameters and  $\chi_q$  terms in the second summation above are chosen so that this entire term vanishes as the electron coordinate goes to  $\infty$ . 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. 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 only to 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  $\mathcal{L}^2$  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<sup>71,72</sup>. 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 breakup 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.

## [H2] 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<sup>73</sup>. The original idea, developed by the mathematician Barry Simon (Ref.<sup>74</sup>), was to rotate all the electronic coordinates by a complex phase factor  $\theta$  as  $r \rightarrow r \exp i\theta$ .

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 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<sup>75</sup>. 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 (see Refs<sup>76-78</sup> and references therein.) 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  $\lambda$  and  $\eta$  are arbitrary parameters to perform the scaling. In smooth exterior complex scaling, one uses a transformation such as,

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

If a complete basis set expansion is used to solve the Schrödinger equation, the exact solution is independent of  $\theta$  and  $\eta$ . In numerical calculations  $\theta$  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 which use only  $\mathcal{L}^2$  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.<sup>76–78</sup>

One notable success of the approach has been its application to computing impact ionization amplitudes for electrons on the hydrogen atom<sup>73</sup>. 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<sup>79</sup>, 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.

## [H2] 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<sup>80–82</sup>, 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  $r \leq a$ . It is assumed that exchange vanishes beyond that region and only local interactions remain.

By diagonalizing the Schrödinger equation in this internal region ( $r \leq a$ ), one obtains a set of discrete states which 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 used basis sets with a fixed boundary condition on the R-matrix surface.<sup>83,84</sup> Later work showed how to relax the fixed boundary condition and extend the method to molecular targets<sup>85–93</sup>. For in-depth reviews see Refs<sup>94–96</sup>. 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<sup>97–100</sup>.

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,

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

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

Here  $H_{N+1}$  is the  $N + 1$  electron Hamiltonian,  $E$  is the energy and  $L_{N+1}$  is the Bloch operator<sup>101</sup> which 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,

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

which satisfies the following eigenvalue problem,

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

Here  $\chi_q$  are a set of  $(N + 1)$  electron correlation 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.<sup>102</sup> was used to ameliorate the problem.

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

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

$$\mathcal{R}_{c,d} = \frac{1}{2} \sum_k \frac{u_{ck}(a) u_{dk}(a)}{[E_k(R) - E(R)]} \quad (10b)$$

$$u_c(a) = \sum_i a_{ci,k} u_{ci}^0(a). \quad (10c)$$

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<sup>102</sup> 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 (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 multi-center 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 which remove the contributions between  $r = a$  and  $r = \infty$  for diffuse Gaussians which are needed to represent the scattering orbitals<sup>93</sup> This procedure is straightforward since for most of these integrals multipole expansions are sufficient. For atomic R-matrix calculations both numerical, B-spline and FE orbitals have been successfully used.<sup>103, 104</sup>

The R-matrix method may be generalized to include the effects of nuclear excitation and even dissociation. The interested reader should consult Refs<sup>92</sup> 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.<sup>81, 105, 106</sup>

To obtain the final solution to (10a), it 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.<sup>107-109</sup> The idea is basically to apply the R-matrix for a series of sub-regions from  $r = a$  to where the potential may be neglected. In each of these sub-regions, 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 which 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<sup>50</sup>. 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<sup>110</sup>, 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.<sup>111,112</sup> 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<sup>113</sup>. In the present context, quantum defect theory explores the behavior 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<sup>114</sup>. Stated in a somewhat 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.

## [H2] 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.<sup>94-96</sup> On the molecular front, theoretical studies have been conducted on photoionization of NO (Ref.<sup>115</sup>), NO<sub>2</sub> (Refs<sup>116,117</sup>), N<sub>2</sub> (Refs<sup>118,119</sup>), Methane<sup>119</sup>, endohedral fullerenes Xe@C60 (Ref.<sup>120</sup>), and CO<sub>2</sub>(Ref.<sup>121</sup>). Electron scattering from N<sub>2</sub> and CO<sub>2</sub>, are the best known systems and show good agreement with experimental results and calculations performed by multiple groups.<sup>119,121,122</sup>

For atomic targets, the Belfast R-matrix codes, whose development began in the 1970s, are being used world-wide 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<sup>123</sup>, to a number of interesting systems. This code uses a set of nonorthogonal 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<sup>124</sup> as a first order correction. Recent calculations using this code include the electron impact excitation of Zn (Ref.<sup>125</sup>), the single and double photoionization of Ne (Ref.<sup>126</sup>), electron-impact excitation and ionization of atomic calcium.<sup>127</sup>

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.<sup>128-130</sup> RMT has also been applied to double-photoionization of He<sup>129</sup>, and photodetachment of F<sup>-</sup> in strong, circularly polarized laser fields.<sup>131,132</sup>

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<sup>3+</sup>, N IV (Ref.<sup>133</sup>), and Fe II (Refs<sup>134,135</sup>).

## [H2] Kohn variational method

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

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 behavior. 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 K, T or S 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 express a variationally corrected K, T or S 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.<sup>137-143</sup>

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

$$\psi(0) = 0 \tag{11}$$

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

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  $\lambda = K, T$  or  $S$  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  $S$  matrix 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<sup>140</sup>. Given the functional

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

its variation is examined by,

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

The third term is neglected to first order accuracy. The first term is zero. If  $\delta \psi = \psi - \psi^t$  where  $\psi^t$  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  $\psi$  is the exact solution to the differential equation, yields,<sup>144</sup>

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

where

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

is the Wronskian. Therefore,

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

and from here one obtains the Kato identity<sup>140,145</sup>

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

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

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

where  $\phi_i(r)$  are a set of  $\mathcal{L}^2$  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,

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

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

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

This formalism incorporates the bound state subspace into the continuum subspace using partitioning. Substituting (19) into (18) and using (20) plus,

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

yields a very compact expression for the variationally corrected quantity,

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



The generalization to the full multi-channel problem is straightforward. The trial function is,

$$\Psi^c = \sum_{c'} \mathcal{A}[\psi_{c'} F_{c'}^c] + \sum_i d_i \chi_i, \quad (23)$$

where  $\psi_{c'}$  are a set of N-particle target states,  $F_{c'}^c$  a single-particle function that describes the scattered particle and  $\chi_i$  a set of (N+1)-particle antisymmetric  $\mathcal{L}^2$  states. The operator  $\mathcal{A}$  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 Eq.(12) that are linearly independent continuum orbitals and are regular at the origin. The generalization of the variational principle to the multichannel case is,

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

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

## [H2] 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 inter-channel coupling correlation effects in the valence photoionization dynamics of SF<sub>6</sub> with good agreement between the two calculations and the experimental results.<sup>146</sup> This study revealed the importance of inter-channel 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 low energy electron impact,<sup>147</sup> experimental and theoretical investigations of the dynamics of dissociative electron attachment to methane,<sup>148</sup> hole localization in K-shell and core-valence-excited acetylene photoionization,<sup>149</sup> photoelectron angular distributions for core ionization of ethane, carbon tetrafluoride and 1,1-difluoroethylene (Ref.<sup>150</sup>), 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 multiphoton 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 ultraviolet and infrared-light pulses.<sup>151</sup>

A final example involves computational studies of positronium (Ps) scattering off of hydrogen. This is a very difficult problem which 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%.<sup>152</sup> In Ref.<sup>153</sup> a study was conducted on Ps-H, e<sup>-</sup>-H and e<sup>+</sup>-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.

## [H1] 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.<sup>123</sup> 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<sup>94,103</sup>, 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<sup>154</sup> 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<sup>95</sup> and the complex Kohn variational method<sup>136</sup>. The former grew out of the Belfast atomic R-matrix codes<sup>155</sup> which were preceded by earlier efforts<sup>156</sup>. The early complex Kohn work was initiated at Los Alamos National Laboratory<sup>138,141</sup> and many of the subsequent and important developments came from the Lawrence Berkeley Laboratory/UC Davis group.<sup>140</sup>

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.

## [H1] 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 will concentrate on methods which approximate the exact propagator,

$$\hat{U}(t; t_0) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n T[\mathbf{H}(t_1)\mathbf{H}(t_2) \cdots \mathbf{H}(t_n)], \quad (25)$$

where  $T$  is the time ordering operator. Here  $\hat{U}(t; t_0)$  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 ( $\delta t$ ) the time ordering operator may be neglected and one gets,

$$\hat{U}(t_0 + \delta t; t_0) \approx \int_{t_0}^{(t_0 + \delta t)} \exp -i[\mathbf{H}(t)t] dt \quad (26)$$

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<sup>157</sup>. If the integral is approximated using the midpoint rule, one obtains,

$$\hat{U}(t_0 + \delta t; t_0) \approx \exp \left( -i[\mathbf{H}(t_0 + \frac{\delta t}{2})] \delta t \right) \quad (27)$$

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 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<sup>158</sup>, approximates the exponential as a Padé approximate,

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

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

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

In practice, the composite exponential is ‘split’ into simpler parts and the Padé approximation applied to the separate parts in order 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<sup>159</sup> (see 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  $\mathcal{L}^2$  basis with time-dependent coefficients and reduce the problem to a set of coupled, time-dependent algebraic equations which 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<sup>160</sup>. 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<sup>161</sup> and orbital adaptive time-dependent coupled-cluster<sup>162</sup>, where variational principles are applied to a N-body wavefunction ansatz; configuration interaction (CI) methods with single excitation<sup>163</sup>, which is effectively a one-electron theory with coupled channels; Complete-Active-Space Self-Consistent-Field methods<sup>164</sup>, where both the CI coefficients and the shape of the orbitals are variationally optimized; Time-Dependent R-matrix methods<sup>130,165</sup>, 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.

## References

1. Hartree, D. R. On some approximate numerical applications of Bohr’s theory of spectra. *Proc. Camb. Phil. Soc.* **21**, 625–641 (1923).
2. Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. *Proc. Camb. Phil. Soc.* **24**, 89–110, DOI: [10.1017/s0305004100011920](https://doi.org/10.1017/s0305004100011920) (1928).
3. Slater, J. C. Note on Hartree’s Method. *Phys. Rev.* **35**, 210–211, DOI: <https://doi.org/10.1103/PhysRev.35.210.2> (1930).
4. Fock, V. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Phys.* **61**, 126–148, DOI: [10.1007/BF01340294](https://doi.org/10.1007/BF01340294) (1930).
5. Zangwill, A. Hartree and Thomas: the forefathers of density functional theory. *Arch. for Hist. Exact Sci.* **67**, 331–348, DOI: [10.1007/s00407-013-0114-4](https://doi.org/10.1007/s00407-013-0114-4) (2013).
6. Hartree, D. R. The Bush differential analyser and its applications. *Nature* **146**, 319–323, DOI: [10.1038/146319a0](https://doi.org/10.1038/146319a0) (1940).
7. Roothaan, C. C. J. New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.* **23**, 69–89, DOI: [10.1103/RevModPhys.23.69](https://doi.org/10.1103/RevModPhys.23.69) (1951).
8. Hall, G. G. The molecular orbital theory of chemical valency VIII. A method of calculating ionization potentials. *Proc. Roy. Soc. A* **205**, 541–552, DOI: [10.1098/rspa.1951.0048](https://doi.org/10.1098/rspa.1951.0048) (1951).
9. Parr, R. G. & Mulliken, R. S. LCAO self-consistent field calculation of the  $\pi$ -electron energy levels of cis- and trans-1,3-butadiene. *J. Chem. Phys.* **18**, 1338–1346, DOI: [10.1063/1.1747474](https://doi.org/10.1063/1.1747474) (1950).

10. Roothaan, C. C. J. Self-Consistent Field Theory for Open Shells of Electronic Systems. *Rev. Mod. Phys.* **32**, 179–185, DOI: [10.1103/RevModPhys.32.179](https://doi.org/10.1103/RevModPhys.32.179) (1960).
11. Pople, J. A. & Nesbet, R. K. Self-Consistent Orbitals for Radicals. *J. Chem. Phys.* **22**, 571–572, DOI: [10.1063/1.1740120](https://doi.org/10.1063/1.1740120) (1954).
12. Piper, W. W. & Prener, J. S. Hartree-Fock Wave Functions for Mn<sup>4+</sup>. *Phys. Rev.* **100**, 1250(A) (1955).
13. Rotenberg, M. Nuclear Hartree-Fock Calculations. *Phys. Rev.* **100**, 439–440, DOI: <https://doi.org/10.1103/PhysRev.100.439> (1955).
14. Heitler, W. & London, F. Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik. *Z. Phys.* **44**, 455–472, DOI: [10.1007/BF01397394](https://doi.org/10.1007/BF01397394) (1927).
15. James, H. M. & Coolidge, A. S. The Ground State of the Hydrogen Molecule. *J. Chem. Phys.* **1**, 825–835, DOI: [10.1063/1.1749252](https://doi.org/10.1063/1.1749252) (1933).
16. Hylleraas, E. A. Über den Grundzustand des Heliumatoms. *Z. Phys.* **48**, 469–494, DOI: [10.1007/BF01340013](https://doi.org/10.1007/BF01340013) (1928).
17. Hylleraas, E. A. Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium. *Z. Phys.* **54**, 347–366, DOI: [10.1007/BF01375457](https://doi.org/10.1007/BF01375457) (1929).
18. Hylleraas, E. A. Über den Grundterm der Zweielektronenprobleme von H-, He, Li+, Be++ usw. *Z. Phys.* **65**, 209–225, DOI: [10.1007/BF01397032](https://doi.org/10.1007/BF01397032) (1930).
19. Hylleraas, E. A. The Schrödinger Two-Electron Atomic Problem. *Adv. Quantum Chem.* **1**, 1–33, DOI: [10.1016/S0065-3276\(08\)60373-1](https://doi.org/10.1016/S0065-3276(08)60373-1) (1964).
20. Kinoshita, T. Ground State of the Helium Atom. *Phys. Rev.* **105**, 1490–1502, DOI: [10.1103/PhysRev.105.1490](https://doi.org/10.1103/PhysRev.105.1490) (1957).
21. Kolos, W. & Roothaan, C. C. J. Accurate electronic wave functions for the H<sub>2</sub> molecule. *Rev. Mod. Phys.* **32**, 219–232, DOI: [10.1103/RevModPhys.32.219](https://doi.org/10.1103/RevModPhys.32.219) (1960).
22. Kolos, W. & Wolniewicz, L. Improved Theoretical Ground-State Energy of the Hydrogen Molecule. *J. Chem. Phys.* **49**, 404–410, DOI: [10.1063/1.1669836](https://doi.org/10.1063/1.1669836) (1968).
23. Sims, J. S. & Hagstrom, S. Combined Configuration-Interaction Hylleraas-Type Wave-Function Study of the Ground State of the Beryllium Atom. *Phys. Rev. A* **4**, 908–916, DOI: [10.1103/PhysRevA.4.908](https://doi.org/10.1103/PhysRevA.4.908) (1971).
24. Sims, J. S. & Hagstrom, S. A. High precision variational calculations for the Born-Oppenheimer energies of the ground state of the hydrogen molecule. *J. Chem. Phys.* **124**, 094101, DOI: [10.1063/1.2173250](https://doi.org/10.1063/1.2173250) (2006).
25. Kellner, G. W. Die Ionisierungsspannung des Heliums nach der Schrödingerschen Theorie. *Z. Phys.* **44**, 91–109, DOI: [10.1007/BF01391720](https://doi.org/10.1007/BF01391720) (1927).
26. Weinbaum, S. The Normal State of the Hydrogen Molecule. *J. Chem. Phys.* **1**, 593–596, DOI: [10.1063/1.1749333](https://doi.org/10.1063/1.1749333) (1933).
27. SHAVITT, I. The history and evolution of configuration interaction. *Mol. Phys.* **94**, 3–17, DOI: [10.1080/00268979809482290](https://doi.org/10.1080/00268979809482290) (1998).
28. David Sherrill, C. & Schaefer, H. F. The Configuration Interaction Method: Advances in Highly Correlated Approaches. In *Adv. Quantum Chem.*, vol. 34, 143–269, DOI: [10.1016/S0065-3276\(08\)60532-8](https://doi.org/10.1016/S0065-3276(08)60532-8) (Academic Press, 1999).
29. Szalay, P. G., Müller, T., Gidofalvi, G., Lischka, H. & Shepard, R. Multiconfiguration Self-Consistent Field and Multireference Configuration Interaction Methods and Applications. *Chem. Rev.* **112**, 108–181, DOI: [10.1021/cr200137a](https://doi.org/10.1021/cr200137a) (2012).
30. Allis, W. P. & Morse, P. M. Theorie der Streuung langsamer Elektronen an Atomen. *Z. Phys.* **70**, 567–582, DOI: [10.1007/BF01340745](https://doi.org/10.1007/BF01340745) (1931).
31. Morse, P. M. Quantum Mechanics of Collision Processes Part II. *Rev. Mod. Phys.* **4**, 577–634, DOI: [10.1103/RevModPhys.4.577](https://doi.org/10.1103/RevModPhys.4.577) (1932).
32. Morse, P. M. & Allis, W. P. The Effect of Exchange on the Scattering of Slow Electrons from Atoms. *Phys. Rev.* **44**, 269–276, DOI: [10.1103/PhysRev.44.269](https://doi.org/10.1103/PhysRev.44.269) (1933).
33. Born, M. & Oppenheimer, R. Zur Quantentheorie der Molekeln. *Annalen der Physik* **389**, 457–484, DOI: [10.1002/andp.19273892002](https://doi.org/10.1002/andp.19273892002) (1927).
34. Hulthén, L. Variational Problem for the Continuous Spectrum of a Schrödinger Equation. *K. Fysiograf. Sällsk. Lund Förhandl* **14(21)**, 1–13 (1944).

35. Hulthén, L. On the Sturm-Liouville Problem Connected with a Continuous Spectrum. *Arkiv f. Mat. Astr. och Fys* **35 A**, No. 25 (1948).
36. Kohn, W. Variational Methods in Nuclear Collision Problems. *Phys. Rev.* **74**, 1763–1772, DOI: <https://doi.org/10.1103/PhysRev.74.1763> (1948).
37. Massey, H. S. W. & Moisewitsch, B. L. Calculation of the 1s-2s Electron Excitation Cross Section of Hydrogen by a Variational Method. *Proc. Phys. Soc. A* **66**, 406–408, DOI: [10.1088/0370-1298/66/4/413](https://doi.org/10.1088/0370-1298/66/4/413) (1953).
38. Moisewitsch, B. L. A variational method for inelastic collision problems. *Phys. Rev.* **82**, 753–753, DOI: [10.1103/PhysRev.82.753.2](https://doi.org/10.1103/PhysRev.82.753.2) (1951).
39. Lippmann, B. A. & Schwinger, J. Variational Principles for Scattering Processes. I. *Phys. Rev.* **79**, 469–480, DOI: [10.1103/PhysRev.79.469](https://doi.org/10.1103/PhysRev.79.469) (1950).
40. Nesbet, R. K. *Variational Methods in Electron-Atom Scattering Theory* (Plenum, New York, 1980).
41. Krausz, F. & Ivanov, M. Attosecond physics. *Rev. Mod. Phys.* **81**, 163–234, DOI: [10.1103/RevModPhys.81.163](https://doi.org/10.1103/RevModPhys.81.163) (2009).
42. Romero, E., Novoderezhkin, V. I. & van Grondelle, R. Quantum design of photosynthesis for bio-inspired solar-energy conversion. *Nature* **543**, 355–365, DOI: [10.1038/nature22012](https://doi.org/10.1038/nature22012) (2017).
43. LeVeque, R. J. *Finite difference methods for ordinary and partial differential equations : steady-state and time-dependent problems* (Society for Industrial and Applied Mathematics, 2007).
44. Boyd, J. P. J. P. *Chebyshev and Fourier spectral methods* (Dover Publications, 2001), 2nd edn.
45. Kopal, Z. *Numerical Analysis* (John Wiley & Sons, Ltd, New York, 1961).
46. Sams, W. N. & Kouri, D. J. Noniterative Solutions of Integral Equations for Scattering. I. Single Channels. *J. Chem. Phys.* **51**, 4809–4814, DOI: [10.1063/1.1671871](https://doi.org/10.1063/1.1671871) (1969).
47. Sams, W. N. & Kouri, D. J. Noniterative Solutions of Integral Equations for Scattering. II. Coupled Channels. *J. Chem. Phys.* **51**, 4815–4819, DOI: [10.1063/1.1671872](https://doi.org/10.1063/1.1671872) (1969).
48. Sams, W. N. & Kouri, D. J. Noniterative Solutions of Integral Equations for Scattering. III. Coupled Open and Closed Channels and Eigenvalue Problems. *J. Chem. Phys.* **52**, 4144–4150, DOI: [10.1063/1.1673622](https://doi.org/10.1063/1.1673622) (1970).
49. Schneider, B. I. & Collins, L. A. Linear-algebraic approach to electron-molecule collisions: Separable exchange approximations. *Phys. Rev. A* **24**, 1264–1266, DOI: [10.1103/PhysRevA.24.1264](https://doi.org/10.1103/PhysRevA.24.1264) (1981).
50. Collins, L. A. & Schneider, B. I. Linear-algebraic approach to electron-molecule collisions: General formulation. *Phys. Rev. A* **24**, 2387, DOI: [10.1103/PhysRevA.24.2387](https://doi.org/10.1103/PhysRevA.24.2387) (1981).
51. Rescigno, T. N. Orthogonality constraints in electron scattering by open-shell targets: Comments on a paper by Riley and Truhlar. *J. Chem. Phys.* **66**, 5255–5257, DOI: [10.1063/1.433761](https://doi.org/10.1063/1.433761) (1977).
52. Rescigno, T. N. & Orel, A. E. Separable approximation for exchange interactions in electron-molecule scattering. *Phys. Rev. A* **24**, 1267–1271, DOI: [10.1103/PhysRevA.24.1267](https://doi.org/10.1103/PhysRevA.24.1267) (1981).
53. Rescigno, T., McCurdy, C. & McKoy, V. Discrete basis set approach to nonspherical scattering. *Chem. Phys. Lett.* **27**, 401–404, DOI: [10.1016/0009-2614\(74\)90251-6](https://doi.org/10.1016/0009-2614(74)90251-6) (1974).
54. Linderberg, J. Finite element methods in quantum mechanics. *Comp. Phys. Rep.* **6**, 209–242, DOI: [10.1016/0167-7977\(87\)90013-X](https://doi.org/10.1016/0167-7977(87)90013-X) (1987).
55. Linderberg, J. Finite elements and partial waves in scattering calculations. *Int. J. Quantum Chem.* **44**, 717–724, DOI: [10.1002/qua.560440863](https://doi.org/10.1002/qua.560440863) (1992).
56. Vincke, M., Malegat, L. & Baye, D. Regularization of singularities in Lagrange-mesh calculations. *J. Phys. B: At. Mol. Phys* **26**, 811–826, DOI: [10.1088/0953-4075/26/5/006](https://doi.org/10.1088/0953-4075/26/5/006) (1993).
57. Rescigno, T. N. & McCurdy, C. W. Numerical grid methods for quantum-mechanical scattering problems. *Phys. Rev. A* **62**, 032706, DOI: [10.1103/PhysRevA.62.032706](https://doi.org/10.1103/PhysRevA.62.032706) (2000).
58. Schneider, B. I. & Collins, L. A. The discrete variable method for the solution of the time-dependent Schrödinger equation. *J. Non-Cryst. Solids* **351**, 1551–1558, DOI: [10.1016/J.JNONCRY SOL.2005.03.028](https://doi.org/10.1016/J.JNONCRY SOL.2005.03.028) (2005).
59. Baye, D. & Heenen, P. H. Generalised meshes for quantum mechanical problems. *J. Phys. A* **19**, 2041–2059, DOI: [10.1088/0305-4470/19/11/013](https://doi.org/10.1088/0305-4470/19/11/013) (1986).
60. Bachau, H., Cormier, E., Decleva, P., Hansen, J. E. & Martín, F. Applications of B-splines in atomic and molecular physics. *Rep. Prog. Phys.* **64**, 1815–1943, DOI: [10.1088/0034-4885/64/12/205](https://doi.org/10.1088/0034-4885/64/12/205) (2001).

61. Rescigno, T. N., Horner, D. A., Yip, F. L. & McCurdy, C. W. Hybrid approach to molecular continuum processes combining Gaussian basis functions and the discrete variable representation. *Phys. Rev. A* **72**, 052709, DOI: [10.1103/PhysRevA.72.052709](https://doi.org/10.1103/PhysRevA.72.052709) (2005).
62. Yip, F. L., McCurdy, C. W. & Rescigno, T. N. Hybrid Gaussian-discrete-variable representation approach to molecular continuum processes: Application to photoionization of diatomic Li<sub>2</sub><sup>+</sup>. *Phys. Rev. A* **78**, 023405, DOI: [10.1103/PhysRevA.78.023405](https://doi.org/10.1103/PhysRevA.78.023405) (2008).
63. Guan, X., Bartschat, K. & Schneider, B. I. Dynamics of two-photon double ionization of helium in short intense xuv laser pulses. *Phys. Rev. A* **77**, 043421, DOI: [10.1103/PhysRevA.77.043421](https://doi.org/10.1103/PhysRevA.77.043421) (2008).
64. Guan, X., Bartschat, K. & Schneider, B. I. Two-photon double ionization of H 2 in intense femtosecond laser pulses. *Phys. Rev. A* **82**, 041404, DOI: [10.1103/PhysRevA.82.041404](https://doi.org/10.1103/PhysRevA.82.041404) (2010).
65. Schneider, B. I. & Collins, L. A. Direct iteration-variation method for scattering problems. *Phys. Rev. A* **33**, 2970, DOI: <https://doi.org/10.1103/PhysRevA.33.2970> (1986).
66. Collins, L. A. & Schneider, B. I. Ab initio methods for electron-molecule collisions. In *Electron-Molecule Scattering and Photoionization*, 147–168 (Springer, Boston, MA, 1988).
67. Burke, P. G. & Schey, H. M. Elastic Scattering of Low-Energy Electrons by Atomic Hydrogen. *Phys. Rev.* **126**, 147–162, DOI: [10.1103/PhysRev.126.147](https://doi.org/10.1103/PhysRev.126.147) (1962).
68. Burke, P. G., Schey, H. M. & Smith, K. Collisions of Slow Electrons and Positrons with Atomic Hydrogen. *Phys. Rev.* **129**, 1258–1274, DOI: [10.1103/PhysRev.129.1258](https://doi.org/10.1103/PhysRev.129.1258) (1963).
69. Smith, K., Miller, W. F. & Mumford, A. J. P. The Elastic and Inelastic Scattering of Electrons and Positrons from the s-states of Atomic Hydrogen. *Phys. Rev.* **76**, 559–564, DOI: [10.1088/0370-1328/76/4/315](https://doi.org/10.1088/0370-1328/76/4/315) (1960).
70. Burke, P. G. & Smith, K. The Low-Energy Scattering of Electrons and Positrons by Hydrogen Atoms. *Rev. Mod. Phys.* **34**, 458–502, DOI: [10.1103/RevModPhys.34.458](https://doi.org/10.1103/RevModPhys.34.458) (1962).
71. Bray, I. & Stelbovics, A. T. Convergent close-coupling calculations of electron-hydrogen scattering. *Phys. Rev. A* **46**, 6995–7011, DOI: [10.1103/PhysRevA.46.6995](https://doi.org/10.1103/PhysRevA.46.6995) (1992).
72. Bray, I. Close-Coupling Theory of Ionization: Successes and Failures. *Phys. Rev. Lett.* **78**, 4721–4724, DOI: [10.1103/PhysRevLett.78.4721](https://doi.org/10.1103/PhysRevLett.78.4721) (1997).
73. McCurdy, C. W., Baertschy, M. & Rescigno, T. N. Solving the three-body Coulomb breakup problem using exterior complex scaling. *J. Phys. B: At. Mol. Phys.* **37**, R137–R187, DOI: [10.1088/0953-4075/37/17/R01](https://doi.org/10.1088/0953-4075/37/17/R01) (2004).
74. Simon, B. Resonances in n-Body Quantum Systems With Dilatation Analytic Potentials and the Foundations of Time-Dependent Perturbation Theory. *Ann. Math.* **97**, 247, DOI: [10.2307/1970847](https://doi.org/10.2307/1970847) (1973).
75. Simon, B. The definition of molecular resonance curves by the method of exterior complex scaling. *Phys. Lett. A* **71**, 211–214, DOI: [10.1016/0375-9601\(79\)90165-8](https://doi.org/10.1016/0375-9601(79)90165-8) (1979).
76. McCurdy, C. W., Stroud, C. K. & Wisinski, M. K. Solving the time-dependent Schrödinger equation using complex-coordinate contours. *Phys. Rev. A* **43**, 5980–5990, DOI: [10.1103/PhysRevA.43.5980](https://doi.org/10.1103/PhysRevA.43.5980) (1991).
77. Scrinzi, A. Infinite-range exterior complex scaling as a perfect absorber in time-dependent problems. *Phys. Rev. A* **81**, 053845, DOI: [10.1103/PhysRevA.81.053845](https://doi.org/10.1103/PhysRevA.81.053845) (2010).
78. Weinmüller, M., Weinmüller, M., Rohland, J. & Scrinzi, A. Perfect absorption in Schrödinger-like problems using non-equidistant complex grids. *J. Comp. Phys.* **333**, 199–211, DOI: [10.1016/j.jcp.2016.12.029](https://doi.org/10.1016/j.jcp.2016.12.029) (2017).
79. Xiaoye, S. L. An Overview of {SuperLU}: Algorithms, Implementation, and User Interface. *ACM Trans. Math. Softw.* **31**, 302 (2005).
80. Wigner, E. P. Resonance reactions. *Phys. Rev.* **70**, 606–618, DOI: [10.1103/PhysRev.70.606](https://doi.org/10.1103/PhysRev.70.606) (1946).
81. Wigner, E. P. & Eisenbud, L. Higher Angular Momenta and Long Range Interaction in Resonance Reactions. *Phys. Rev.* **72**, 29–41, DOI: [10.1103/PhysRev.72.29](https://doi.org/10.1103/PhysRev.72.29) (1947).
82. Lane, A. M. & Thomas, R. G. R-Matrix Theory of Nuclear Reactions. *Rev. Mod. Phys.* **30**, 257–353, DOI: [10.1103/RevModPhys.30.257](https://doi.org/10.1103/RevModPhys.30.257) (1958).
83. Burke, P. G., Hibbert, A. & Robb, W. D. Electron scattering by complex atoms. *J. Phys. B: At. Mol. Phys.* **4**, 153–161, DOI: [10.1088/0022-3700/4/2/002](https://doi.org/10.1088/0022-3700/4/2/002) (1971).

84. Burke, P. G. & Robb, W. D. Elastic scattering of electrons by hydrogen and helium atoms. *J. Phys. B: At. Mol. Phys.* **5**, 44–54, DOI: [10.1088/0022-3700/5/1/014](https://doi.org/10.1088/0022-3700/5/1/014) (1972).
85. Schneider, B. R-matrix theory for electron-atom and electron-molecule collisions using analytic basis set expansions. *Chem. Phys. Lett.* **31**, 237–241 (1975).
86. Schneider, B. I. R-matrix theory for electron-molecule collisions using analytic basis set expansions. II. Electron-H 2 scattering in the static-exchange model. *Phys. Rev. A* **11**, 1957 (1975).
87. Schneider, B. I. & Hay, P. J. Elastic scattering of electrons from F 2: An R-matrix calculation. *Phys. Rev. A* **13**, 2049 (1976).
88. Schneider, B. I. & Hay, P. J. Elastic scattering of electrons from F2. *J. Phys. B: At. Mol. Phys.* **9**, L165 (1976).
89. Schneider, B. I., Le Dourneuf, M. & Lan, V. K. Resonant vibrational excitation of diatomic molecules by electron impact. An ab initio R-matrix calculation for e–N<sub>2</sub>. In *Physics of Electronic and Atomic Collisions: ICPEAC XI*, 292 (1979).
90. Schneider, B. I., Le Dourneuf, M. & Lan, V. K. Resonant vibrational excitation of N 2 by low-energy electrons: an ab initio R-matrix calculation. *Phys. Rev. Lett.* **43**, 1926 (1979).
91. Schneider, B. I. The R-Matrix Method for Electron-Molecule Scattering: Theory and Computation. In *Electron-Molecule and Photon-Molecule Collisions*, 77–86 (Springer, Boston, MA, 1979).
92. LeDourneuf, M., Schneider, B. I. & Burke, P. G. Theory of vibrational excitation and dissociative attachment: an R-matrix approach. *J. Phys. B: At. Mol. Phys.* **12**, L365–L369, DOI: [10.1088/0022-3700/12/12/008](https://doi.org/10.1088/0022-3700/12/12/008) (1979).
93. Tennyson, J. & Morgan, L. A. Electron collisions with polyatomic molecules using the R-matrix method. *Phil. Trans. Roy. Soc. A* **357**, 1161–1173, DOI: [10.1098/rsta.1999.0369](https://doi.org/10.1098/rsta.1999.0369) (1999).
94. Burke, P. G. *R-Matrix Theory of Atomic Collisions Application to Atomic, Molecular and Optical Processes* (Springer-Verlag Berlin Heidelberg, 2011).
95. Tennyson, J. Electron–molecule collision calculations using the R-matrix method. *Phys. Reports* **491**, 29–76, DOI: [10.1016/j.physrep.2010.02.001](https://doi.org/10.1016/j.physrep.2010.02.001) (2010).
96. Descouvemont, P. & Baye, D. The R-matrix theory. *Rep. Prog. Phys.* **73**, 036301, DOI: [10.1088/0034-4885/73/3/036301](https://doi.org/10.1088/0034-4885/73/3/036301) (2010).
97. Szmytkowski, R. Variational R-matrix methods for many-electron systems: Unified relativistic theory. *Phys. Rev. A* **63**, 14, DOI: [10.1103/PhysRevA.63.062704](https://doi.org/10.1103/PhysRevA.63.062704) (2001).
98. Grant, I. P. The Dirac operator on a finite domain and the R -matrix method. *J. Phys. B: At. Mol. Phys* **41**, 055002, DOI: [10.1088/0953-4075/41/5/055002](https://doi.org/10.1088/0953-4075/41/5/055002) (2008).
99. Grineviciute, J. & Halderson, D. Relativistic R matrix and continuum shell model. *Phys. Rev. C* **85**, 1–6, DOI: [10.1103/PhysRevC.85.054617](https://doi.org/10.1103/PhysRevC.85.054617) (2012).
100. Baye, D. Calculable R-matrix method for the Dirac equation. *Phys. Rev. A* **92**, 042112, DOI: [10.1103/PhysRevA.92.042112](https://doi.org/10.1103/PhysRevA.92.042112) (2015).
101. Bloch, C. Une formulation unifiée de la théorie des réactions nucléaires. *Nuc. Phys.* **4**, 503–528, DOI: [10.1016/0029-5582\(87\)90058-7](https://doi.org/10.1016/0029-5582(87)90058-7) (1957).
102. Buttle, P. J. A. Solution of Coupled Equations by R -Matrix Techniques. *Phys. Rev.* **160**, 719–729, DOI: [10.1103/PhysRev.160.719](https://doi.org/10.1103/PhysRev.160.719) (1967).
103. Zatsarinny, O. BSR: B-spline atomic R-matrix codes. *Comp. Phys. Commun.* **174**, 273–356, DOI: [10.1016/j.cpc.2005.10.006](https://doi.org/10.1016/j.cpc.2005.10.006) (2006).
104. Mašín, Z. & Gorfinkiel, J. D. Towards an accurate representation of the continuum in calculations of electron, positron and laser field interactions with molecules. *J. Phys. Conf. Ser.* **490**, 012090, DOI: [10.1088/1742-6596/490/1/012090](https://doi.org/10.1088/1742-6596/490/1/012090) (2014).
105. Kapur, P., & Peierls, R. The dispersion formula for nuclear reactions. *Proc. Roy. Soc. A* **166**, 277–295, DOI: [10.1098/rspa.1938.0093](https://doi.org/10.1098/rspa.1938.0093) (1938).
106. Siegert, A. J. F. On the Derivation of the Dispersion Formula for Nuclear Reactions. *Phys. Rev.* **56**, 750–752, DOI: [10.1103/PhysRev.56.750](https://doi.org/10.1103/PhysRev.56.750) (1939).
107. Light, J. C. & Walker, R. B. An R matrix approach to the solution of coupled equations for atom-molecule reactive scattering. *J. Chem. Phys.* **65**, 4272–4282, DOI: [10.1063/1.432836](https://doi.org/10.1063/1.432836) (1976).

108. Schneider, B. I. & Taylor, H. S. The solution of driven equations by R-matrix propagation methods. *J. Chem. Phys* **77**, 379–382, DOI: [10.1063/1.443616](https://doi.org/10.1063/1.443616) (1982).
109. Baluja, K. L., Burke, P. G. & Morgan, L. A. and L.A. MORGAN. *Comp. Phys. Commun.* **27**, 299–307 (1982).
110. Axelsson, O. *Iterative solution methods* (Cambridge University Press, 1994).
111. Berrington, K. A. & Ballance, C. P. Partitioned R-matrix theory. *J. Phys. B: At. Mol. Phys* **35**, 2275, DOI: [10.1088/0953-4075/35/10/307](https://doi.org/10.1088/0953-4075/35/10/307) (2002).
112. Tennyson, J. Partitioned R-matrix theory for molecules. *J. Phys. B: At. Mol. Phys.* **37**, 1061–1071, DOI: [10.1088/0953-4075/37/5/009](https://doi.org/10.1088/0953-4075/37/5/009) (2004).
113. Lane, A. M. The application of Wigner's R-matrix theory to atomic physics. *J. Phys. B: At. Mol. Phys.* **19**, 253–257, DOI: [10.1088/0022-3700/19/2/014](https://doi.org/10.1088/0022-3700/19/2/014) (1986).
114. Lucchese, R. R., Rescigno, T. N. & McCurdy, C. W. The Connection between Resonances and Bound States in the Presence of a Coulomb Potential. *J. Phys. Chem. A* **123**, 85–95, DOI: <https://doi.org/10.1021/acs.jpca.8b10715> (2018).
115. Tashiro, M. Theoretical treatment of molecular photoionization based on the R-matrix method. *J. Phys. Conf. Ser* **388**, 022077, DOI: [10.1088/1742-6596/388/2/022077](https://doi.org/10.1088/1742-6596/388/2/022077) (2012).
116. Ilchen, M. *et al.* Photoelectron angular distribution studies of the outer valence states of N<sub>2</sub>. *J. Phys. B: At. Mol. Phys* **45**, 225102, DOI: [10.1088/0953-4075/45/22/225102](https://doi.org/10.1088/0953-4075/45/22/225102) (2012).
117. Brambila, D. S., Harvey, A. G., Mašín, Z., Gorfinkiel, J. D. & Smirnova, O. The role of multichannel effects in the photoionization of the NO<sub>2</sub> molecule: an ab initio R-matrix study. *J. Phys. B* **48**, 245101, DOI: [10.1088/0953-4075/48/24/245101](https://doi.org/10.1088/0953-4075/48/24/245101) (2015).
118. VanGyseghem, G., Gorczyca, T. W. & Ballance, C. P. Near-Threshold Photoionization of Molecular Nitrogen. *J. Phys. Conf. Ser* **635**, 112102, DOI: [10.1088/1742-6596/635/11/112102](https://doi.org/10.1088/1742-6596/635/11/112102) (2015).
119. Brigg, W. J. *et al.* Calculated photoionization cross sections using Quantemol-N. *Jpn. J. Appl. Phys* **54**, 06GA02, DOI: [10.7567/JJAP.54.06GA02](https://doi.org/10.7567/JJAP.54.06GA02) (2015).
120. Gorczyca, T. W., Hasoglu, M. F. & Manson, S. T. Photoionization of endohedral atoms using R -matrix methods: Application to Xe@C 60. *Phys. Rev. A* **86**, 033204, DOI: [10.1103/PhysRevA.86.033204](https://doi.org/10.1103/PhysRevA.86.033204) (2012).
121. Rouzée, A. *et al.* Imaging the electronic structure of valence orbitals in the XUV ionization of aligned molecules. *J. Phys. B: At. Mol. Phys* **47**, 124017, DOI: [10.1088/0953-4075/47/12/124017](https://doi.org/10.1088/0953-4075/47/12/124017) (2014).
122. Plésiat, E., Decleva, P. & Martín, F. Vibrational branching ratios in the photoelectron spectra of N<sub>2</sub> and CO: interference and diffraction effects. *Phys. Chem. Chem. Phys.* **14**, 10853, DOI: [10.1039/c2cp40693d](https://doi.org/10.1039/c2cp40693d) (2012).
123. Zatsarinny, O. & Bartschat, K. The B-spline R-matrix method for atomic processes: application to atomic structure, electron collisions and photoionization. *J. Phys. B: At. Mol. Phys.* **46**, 112001, DOI: [10.1088/0953-4075/46/11/112001](https://doi.org/10.1088/0953-4075/46/11/112001) (2013).
124. Bethe, H. A. & Salpeter, E. E. *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).
125. Bartschat, K. *et al.* Effect of cascade transitions on the polarization of light emitted after electron-impact excitation of Zn by spin-polarized electrons. *Phys. Rev. A* **100**, 012702, DOI: [10.1103/PhysRevA.100.012702](https://doi.org/10.1103/PhysRevA.100.012702) (2019).
126. Chen, Z. *et al.* Pulse-duration dependence of the double-to-single ionization ratio of Ne by intense 780-nm and 800-nm laser fields: Comparison of simulations with experiments. *Phys. Rev. A* **99**, 043408, DOI: [10.1103/PhysRevA.99.043408](https://doi.org/10.1103/PhysRevA.99.043408) (2019).
127. Zatsarinny, O., Parker, H. & Bartschat, K. Electron-impact excitation and ionization of atomic calcium at intermediate energies. *Phys. Rev. A* **99**, 012706, DOI: [10.1103/PhysRevA.99.012706](https://doi.org/10.1103/PhysRevA.99.012706) (2019).
128. Ó Broin, C. & Nikolopoulos, L. A. A. R-matrix-incorporating-time method for H<sub>2</sub><sup>+</sup> in short and intense laser fields. *Phys. Rev. A* **92**, 063428, DOI: [10.1103/PhysRevA.92.063428](https://doi.org/10.1103/PhysRevA.92.063428) (2015).
129. Clarke, D. D. A., Armstrong, G. S. J., Brown, A. C. & van der Hart, H. W.  $R$ -matrix-with-time-dependence theory for ultrafast atomic processes in arbitrary light fields. *Phys. Rev. A* **98**, 053442, DOI: [10.1103/PhysRevA.98.053442](https://doi.org/10.1103/PhysRevA.98.053442) (2018).
130. Brown, A. *et al.* RMT: R-matrix with time-dependence. Solving the semi-relativistic, time-dependent Schrodinger equation for general, multi-electron atoms and molecules in intense, ultrashort, arbitrarily polarized laser pulses. *arXiv:1905.06156v1* (2019).



131. Hassouneh, O., Law, S., Shearer, S. F. C., Brown, A. C. & van der Hart, H. W. Electron rescattering in strong-field photodetachment of F-. *Phys. Rev. A* **91**, 031404, DOI: [10.1103/PhysRevA.91.031404](https://doi.org/10.1103/PhysRevA.91.031404) (2015).
132. Armstrong, G. S., Clarke, D. D., Brown, A. C. & Van Der Hart, H. W. Electron rotational asymmetry in strong-field photodetachment from F- by circularly polarized laser pulses. *Phys. Rev. A* **99**, 1–9, DOI: [10.1103/PhysRevA.99.023429](https://doi.org/10.1103/PhysRevA.99.023429) (2019).
133. Aggarwal, K. M., Keenan, F. P. & Lawson, K. D. Electron impact excitation of NIV: Calculations with the DARC code and a comparison with ICFT results. *Mon. Notices Royal Astron. Soc.* **461**, 3997–4012, DOI: [10.1093/mnras/stw1369](https://doi.org/10.1093/mnras/stw1369) (2016).
134. Smyth, R. T., Ramsbottom, C. A., Keenan, F. P., Ferland, G. J. & Ballance, C. P. Towards converged electron-impact excitation calculations of low-lying transitions in Fe II. *Mon. Notices Royal Astron. Soc.* **483**, 654–663, DOI: [10.1093/mnras/sty3198](https://doi.org/10.1093/mnras/sty3198) (2018).
135. Ballance, C. P., Loch, S. D., Pindzola, M. S. & Griffin, D. C. Electron-impact excitation and ionization of W<sup>3+</sup> for the determination of tungsten influx in a fusion plasma. *J. Phys. B: At. Mol. Opt. Phys.* **46**, DOI: [10.1088/0953-4075/46/5/055202](https://doi.org/10.1088/0953-4075/46/5/055202) (2013).
136. Rescigno, T., Lengsfeld, B. H., III & McCurdy, C. W. The Incorporation of Modern Electronic Structure Methods in Electron-Molecule Collision Problems: Variational Calculations Using the Complex Kohn Method. In Yarkony, D. (ed.) *Modern Electronic Structure Theory*, chap. 9, 501 (World Scientific Publishing Co., 1995).
137. Schneider, B. I. & Rescigno, T. N. Complex Kohn variational method: Application to low-energy electron-molecule collisions. *Phys. Rev. A* **37**, 3749–3754, DOI: [10.1103/PhysRevA.37.3749](https://doi.org/10.1103/PhysRevA.37.3749) (1988).
138. Rescigno, T. N. & Schneider, B. I. Electron-impact excitation of the b  $3\Sigma^+$  state of H<sub>2</sub> using the complex Kohn method: R dependence of the cross section. *J. Phys. B: At. Mol. Phys.* **21**, L691 (1988).
139. Schneider, B. I., Rescigno, T. N., McCurdy, C. W. & Lengsfeld III, B. H. New developments in the ab initio treatment of low energy electron collisions with molecules. In *AIP Conf. Proce.*, vol. 204, 83–97 (AIP, 1990).
140. Rescigno, T. N., McCurdy, C. W., Orel, A. E. & Lengsfeld, B. H. The Complex Kohn Variational Method. In Huo, W. & Gianturco, F. (eds.) *Computational Methods for Electron–Molecule Collisions*, 1–44, DOI: [10.1007/978-1-4757-9797-8\\_1](https://doi.org/10.1007/978-1-4757-9797-8_1) (Springer US, Boston, MA, 1995).
141. Rescigno, T. N. & Schneider, B. I. Disappearance of continuum exchange integrals from algebraic variational calculations of electron scattering. *Phys. Rev. A* **37**, 1044–1046, DOI: [10.1103/PhysRevA.37.1044](https://doi.org/10.1103/PhysRevA.37.1044) (1988).
142. Rescigno, T. N., McCurdy, C. W. & Schneider, B. I. Accurate ab initio treatment of low-energy electron collisions with polyatomic molecules: Resonant electron-formaldehyde scattering. *Phys. Rev. Lett.* **63**, 248 (1989).
143. Schneider, B. I., Rescigno, T. N., Lengsfeld III, B. H. & McCurdy, C. W. Accurate ab initio treatment of low-energy electron collisions with ethylene. *Phys. Rev. Lett.* **66**, 2728 (1991).
144. Kato, T. Upper and Lower Bounds of Scattering Phases. *Prog. Theo. Phys.* **6**, 394–407, DOI: [10.1143/ptp/6.3.394](https://doi.org/10.1143/ptp/6.3.394) (1951).
145. Kato, T. Variational methods in Collision Problems. *Phys. Rev.* **80**, 475 (1950).
146. Jose, J., Lucchese, R. R. & Rescigno, T. N. Interchannel coupling effects in the valence photoionization of SF<sub>6</sub>. *J. Chem. Phys.* **140**, 204305, DOI: [10.1063/1.4876576](https://doi.org/10.1063/1.4876576) (2014).
147. Rescigno, T. N. & Orel, A. E. Theoretical study of excitation of the low-lying electronic states of water by electron impact. *Phys. Rev. A - At. Mol. Opt. Phys.* **88**, 012703, DOI: [10.1103/PhysRevA.88.012703](https://doi.org/10.1103/PhysRevA.88.012703) (2013).
148. Douguet, N. *et al.* Signatures of bond formation and bond scission dynamics in dissociative electron attachment to methane. *Phys. Chem. Chem. Phys.* **17**, 25621–25628, DOI: [10.1039/C5CP04178C](https://doi.org/10.1039/C5CP04178C) (2015).
149. Rescigno, T. N., Trevisan, C. S. & McCurdy, C. W. Tracking hole localization in K-shell and core-valence-excited acetylene photoionization via body-frame photoelectron angular distributions. *Phys. Rev. A* **91**, 023429, DOI: [10.1103/PhysRevA.91.023429](https://doi.org/10.1103/PhysRevA.91.023429) (2015).
150. Menssen, A. *et al.* Molecular frame photoelectron angular distributions for core ionization of ethane, carbon tetrafluoride and 1,1-difluoroethylene. *J. Phys. B: At. Mol. Opt. Phys.* **49**, 055203, DOI: [10.1088/0953-4075/49/5/055203](https://doi.org/10.1088/0953-4075/49/5/055203) (2016).
151. Douguet, N., Schneider, B. I. & Argenti, L. Application of the complex Kohn variational method to attosecond spectroscopy. *Phys. rev. A* **98**, 23403 (2018).
152. Zhang, J. Y., Yan, Z. C. & Schwingenschlögl, U. Elastic scattering of positronium: Application of the confined variational method. *Epl* **99**, 43001, DOI: [10.1209/0295-5075/99/43001](https://doi.org/10.1209/0295-5075/99/43001) (2012).

153. Van Reeth, P., Woods, D., Ward, S. J. & Humberston, J. W. Corrigendum: Comparison of positronium, positron and electron collisions with hydrogen at low velocities (2016 J. Phys. B: At. Mol. Opt. Phys. 49 114001). *J. Phys. B: At. Mol. Opt. Phys.* **49**, 169501, DOI: [10.1088/0953-4075/49/16/169501](https://doi.org/10.1088/0953-4075/49/16/169501) (2016).
154. Lucchese, R. R. Anomalous singularities in the complex Kohn variational principle of quantum scattering theory. *Phys. Rev. A* **40**, 6879–6885, DOI: [10.1016/B978-0-12-409547-2.04994-5](https://doi.org/10.1016/B978-0-12-409547-2.04994-5) (1989).
155. Burke, P. G. & Robb, W. D. The R-Matrix Theory of Atomic Processes. *Ad. Atom. Molec. Phys.* **11**, 143–214, DOI: [10.1016/S0065-2199\(08\)60030-5](https://doi.org/10.1016/S0065-2199(08)60030-5) (1976).
156. Schneider, B. I. R-Matrix Approach to Electron-Molecule Scattering. In *Physics of Electronic and Atomic Collisions: ICPEAC IX*, 559 (1975).
157. Ndong, M., Tal-Ezer, H., Kosloff, R. & Koch, C. P. A Chebychev propagator with iterative time ordering for explicitly time-dependent Hamiltonians. *J. Chem. Phys.* **132**, 064105, DOI: [10.1063/1.3312531](https://doi.org/10.1063/1.3312531) (2010).
158. Crank, J. & Nicolson, P. Practical Method for Numerical Evaluation of Solutions of partial Differential Equations of the Heat-Conduction Type. *Math. Proc. Camb. Phi. Soc.* **43**, 50–67, DOI: <https://doi.org/10.1017/S0305004100023197> (1947).
159. Lanczos, C. An iteration method for the solution of the eigenvalue problem of linear differential and integral operators. *J. Res. Nat. Bur. Stand.* **45**, 255, DOI: [10.6028/jres.045.026](https://doi.org/10.6028/jres.045.026) (1950).
160. Pindzola, M. S. *et al.* Time-dependent close-coupling calculations of atomic and molecular collision processes. *J. Phys. Conf. Ser* **88**, 012012, DOI: [10.1088/1742-6596/88/1/012012](https://doi.org/10.1088/1742-6596/88/1/012012) (2007).
161. Miyagi, H. & Madsen, L. B. Time-dependent restricted-active-space self-consistent-field theory for laser-driven many-electron dynamics. *Phys. Rev. A* **87**, 062511, DOI: [10.1103/PhysRevA.87.062511](https://doi.org/10.1103/PhysRevA.87.062511) (2013).
162. Kvaal, S. Ab initio quantum dynamics using coupled-cluster. *J. Chem. Phys.* **136**, 194109, DOI: [10.1063/1.4718427](https://doi.org/10.1063/1.4718427) (2012).
163. Greenman, L. *et al.* Implementation of the time-dependent configuration-interaction singles method for atomic strong-field processes. *Phys. Rev. A* **82**, 023406, DOI: [10.1103/PhysRevA.82.023406](https://doi.org/10.1103/PhysRevA.82.023406) (2010).
164. Sato, A. T. & Ishikawa, K. L. Time-dependent complete active-space self-consistent field method for multielectron dynamics in intense laser fields. In *Pacific Rim Conference on Lasers and Electro-Optics, CLEO - Technical Digest*, vol. 88, 023402, DOI: [10.1109/CLEOPR.2013.6600023](https://doi.org/10.1109/CLEOPR.2013.6600023) (American Physical Society, 2013).
165. Moore, L. *et al.* The RMT method for many-electron atomic systems in intense short-pulse laser light. *J. Mod. Opt.* **58**, 1132–1140, DOI: [10.1080/09500340.2011.559315](https://doi.org/10.1080/09500340.2011.559315) (2011).
166. Zatsarinny, O. & Froese Fischer, C. Atomic structure calculations using MCHF and BSR. *Comp. Phys. Commun.* **180**, 2041–2065, DOI: [10.1016/j.cpc.2009.06.007](https://doi.org/10.1016/j.cpc.2009.06.007) (2009).
167. Feshbach, H. Unified Theory of Nuclear Reactions. *Ann. Phys.* **5**, 357–390, DOI: [https://doi.org/10.1016/0003-4916\(58\)90007-1](https://doi.org/10.1016/0003-4916(58)90007-1) (1958).
168. Feshbach, H. Unified Theory of Nuclear Reactions II. *Ann. Phys.* **19**, 287–313, DOI: [10.1006/aphy.2000.6016](https://doi.org/10.1006/aphy.2000.6016) (1962).
169. Paige, C. C. *The computation of eigenvalues and eigenvectors of very large sparse matrices*. Ph.D. thesis, University of London (1971).
170. Cullum, J. K. & Willoughby, R. A. *Lanczos Algorithms for Large Symmetric Eigenvalue Computations, Vol. 1: Theory, Vol. 2: Programs* (Birkhauser, Boston, 1985).
171. Saad, Y. *Iterative methods for sparse linear systems* (SIAM, 2003).
172. Park, T. J. & Light, J. C. Unitary quantum time evolution by iterative Lanczos reduction. *J. Chem. Phys.* **85**, 5870–5876, DOI: [10.1063/1.451548](https://doi.org/10.1063/1.451548) (1986).
173. Tal-Ezer, H. & Kosloff, R. An accurate and efficient scheme for propagating the time dependent Schrödinger equation. *J. Chem. Phys.* **81**, 3967–3971, DOI: [10.1063/1.448136](https://doi.org/10.1063/1.448136) (1984).
174. Leforestier, C. *et al.* A comparison of different propagation schemes for the time dependent Schrödinger equation. *J. Comp. Phys.* **94**, 59–80, DOI: [10.1016/0021-9991\(91\)90137-A](https://doi.org/10.1016/0021-9991(91)90137-A) (1991).

## Acknowledgements

This work was supported by the National Institute of Standards and Technology (NIST). HG acknowledges support from the National Research Council (NRC) Fellowship Program.

## Author contributions

The authors contributed equally to all aspects of the article.

## Competing interests

The authors declare no competing interests.

## Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

## Peer review information

Nature Reviews Physics thanks Jonathan Tennyson, Andrew Brown and the anonymous reviewer for their contribution to the peer review of this work.

### 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 close-coupling, the R-matrix method and the Kohn variational method 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.

## 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 which 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<sup>94</sup>.

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 which 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 following example.

## Box 2 Fredholm to Volterra integral equations

Consider the following Fredholm integral equation of the second kind,

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

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

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

Introduction of quadratures directly into (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 (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,

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

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

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,

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

is determined, the solution to  $u$  is,

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

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

$$U(r|r') = \sum_i u_i(r)\phi_i(r') \quad (34)$$

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.

## 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 to compute the Hamiltonian matrices of the operator  $[H_{N+1}(\mathbf{r}; \mathbf{R}) + L_{N+1}]$ . 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<sup>103,166</sup>. 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  $i$ 'th 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  $\mathbf{r}_i$  are the sector R-matrices for region  $i$ . Using equations (35), (36) and (37) and that 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,

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

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.

## Box 4 Kohn method practical numerical issues

In the full multi-channel 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,

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

where  $f_{c'}$  and  $g_{c'}$  are the free orbitals,  $\phi_i^{c'}$  are the bound functions, and  $\alpha$ ,  $\lambda$  and  $\delta$  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  $\Theta_c$  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  $\Theta_c$  contains one or more determinants containing the added  $\phi_i^c$  orbital and those which 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<sup>167,168</sup>. In contrast to the single channel case, the  $P$ -space part of the multi-channel 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 hydrogen atom. The appropriate term to include in  $Q$ -space in this case is the  $|1s^2\rangle$  term<sup>51</sup>. Other terms that belong to  $Q$ -space in this example are terms of the form  $|\phi_i \phi_j\rangle$  where  $i$  runs over all indices except  $1s$ . What remains in the  $P$ -space are then terms of the form  $|1s \phi_i\rangle$  where  $\phi_i$  is not  $1s$ .

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

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

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  $\chi_i$  functions and  $V_{opt}$  is the optical potential.

The multichannel form of Eq. 22 is<sup>40,140</sup>

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

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,

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

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  $H_{\text{eff}}$ , which are readily computed with electronic structure codes.

## 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<sup>159,169,170</sup>. The method requires the application of an often large, but sparse matrix to a vector. Specific routines which 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,  $\mathbf{H}_{m \times m}^{(\Lambda)}$  tridiagonal matrix, where ideally  $m \ll n$  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<sup>110,170,171</sup>. To circumvent linear dependence often requires additional and expensive re-orthogonalization procedures.

The transformation between the two representations is given by:

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

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

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

where,

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

The vectors in Eq.(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<sup>157,172-174</sup>. 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,  $|q_2\rangle \dots |q_m\rangle$ , 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 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,  $\hat{\mathbf{U}}$ , may be approximated as

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

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,

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

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

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

## Glossary terms

- **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.
- **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.
- **Born-Oppenheimer approximation:** An approximation in molecular systems that treats electronic and nuclear motion adiabatically. This assumption is based on difference in time-scales of electronic and nuclear motions. Consequently, the electronic wavefunction can be computed by freezing the positions of the nuclei. Repeating this calculation as a parametric function of nuclear positions produces a potential in which the nuclei move.
- **Padé approximate:** A numerical method that approximates a function by a rational function of two polynomials.
- **Configuration interaction:** A quantum chemical variational method for solving 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 large number of configurations force the truncation of the expansions.
- **Coupled cluster:** 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 non-linear equations.
- **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.
- **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 electron partially screen the bare nuclear charge.
- **Re-arrangement collisions:** are collisions in which the initial and final states are eigenstates of different unperturbed Hamiltonians.
- **S, T, and K-matrix:** 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. For exact definitions and relations refer to Ref.<sup>94</sup>
- **R-matrix:** “The R-matrix relates the reduced radial wave function  $F_i(r)$ , describing the radial motion of the scattered electron in the  $i$ th channel, to its derivative on the boundary  $r = a_0$  by the equation:”<sup>94</sup>

$$F_i(a_0) = \sum_j R_{ij}(E) a_0 dF_j/dr|_{r=a_0}$$

**TOC blurb:** Numerical methods such as close-coupling, R-matrix, the Kohn variational method have been around for decades, but more recently they have been applied to the treatment of the time-dependent interaction of strong electromagnetic fields with atoms and molecules.