The RMT method for describing many-electron atoms in intense short laser pulses

M A Lysaght¹, L R Moore¹, L A A Nikolopoulos², J S Parker¹, H W van der Hart¹ and K T Taylor¹
¹ Centre for Theoretical Atomic, Molecular and Optical Physics, School of Mathematics and Physics, Queen’s University Belfast, Belfast, BT7 1NN, UK
² School of Physical Sciences, Dublin City University, Dublin 9, Ireland
E-mail: michael.lysaght@ichec.ie

Abstract. We describe how we have extended the underlying methods of the HELIUM code to describe multi-electron systems exposed to intense short-pulse laser light. We achieve this extension through exploiting the powerful R-matrix division-of-space concept to bring together a numerical method (basis set) most appropriate to the multi-electron finite inner region and a different numerical method (finite difference) most appropriate to the one-electron outer region. In order for the method to exploit massively parallel supercomputers efficiently, we time-propagate the wave function in both regions by employing schemes based on the Arnoldi method, long employed in HELIUM.

1. Introduction
The intrinsic time-scale of electron motion in matter is the attosecond time-scale (1 attosecond = $10^{-18}$s) [1] and just as femtosecond (1 femtosecond = $10^{-15}$s) laser technology offers us the means of accessing real-time nuclear dynamics [2], attosecond light pulse technology now promises us the revolutionary ability to measure and control the correlated motion of electrons in atomic systems on their own temporal scale. Recent ground-breaking ultrafast measurements [3, 4] demonstrate that a bottleneck in our understanding of correlated electron dynamics in atoms and molecules is the current state of theory. Correlated electron motion by its very definition is a quantum many-body process and so theory must go beyond the widely used single-particle picture so far employed to good effect to describe single electron dynamics [5].

Currently, the most sophisticated method that goes beyond the single particle model is that underlying the HELIUM code [6]. HELIUM is a pioneering code in the area of Attosecond Science. Not only has it made possible important scientific discovery (afterwards borne out by laboratory experiment) [7] but it has, in doing so, explored the feasibility of propagating accurate solutions of a multi-dimensional TDSE. The code is specifically constructed to describe both single- and double-electron ionization of a two-electron atom or ion exposed to intense laser light. The HELIUM code’s continuing success undoubtedly lies in the fact that, from the start, it was designed around Massively Parallel Processing (MPP) computer architectures [6]. The underlying method of the code combines a high-order Arnoldi time-propagator [8, 6] with Finite Difference (FD) grid techniques. By choosing an appropriate distribution over processors HELIUM involves only nearest neighbour communications which has enabled it to effectively harness the full power of today’s largest supercomputers.
Figure 1. Partition of electron position space. In region I an eigenstate expansion representation of the wavefunction is chosen, while in region II a grid representation is considered. The boundary of region I is at \( r = b \) and the outer boundary of region II is at \( r = R \). The radial variable of the \((N+1)\)-th electron is denoted as \( r \). The grid points in region II are denoted by \( i \), where \( i_b \) is the grid point on the boundary with region I and \( i_R \) is the grid point on the outer region boundary. The spacing between grid points is denoted by \( h \).

With this capability in mind, the designers of the HELIUM code have recently demonstrated the potential to carry over the FD technology of HELIUM into an accurate description of a general many-electron atom exposed to intense light pulses [9, 10]. This carry-over has been shown to be possible by invoking the powerful division-of-space concept central to the highly successful \( R \)-matrix theory of atomic and molecular processes [11]. The division-of-space concept, whereby the position space occupied by the atomic electrons is divided into two separate regions, not only makes possible the integration of FD technology into the description of the ultrafast ionization of many-electron atoms, but also allows an efficient way of limiting the many-electron representation of an atom to the only spatial region where it is absolutely necessary, i.e., a small region close to the nucleus. In this paper we provide an overview of our recent development work and also provide illustrative results that demonstrate the accuracy of the new R-Matrix incorporating Time (RMT) method.

2. The RMT method

Neglecting relativistic effects, the behaviour of a \( N+1 \) electron atomic system in the presence of a laser field is governed by the Time-Dependent Schrödinger Equation (TDSE)

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \Psi(X_{N+1}, t) = H_{N+1}(t) \Psi(X_{N+1}, t),
\]

where the Hamiltonian, \( H_{N+1} \), is given by:

\[
H_{N+1} = \sum_{i=1}^{N+1} \left( \frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \frac{1}{2} \sum_{j=1}^{N+1} \frac{1}{r_{ij}} \right) + \mathbf{E}(t) \cdot \sum_{i=1}^{N+1} \mathbf{r}_i.
\]

In eq.2 we have taken the origin of the coordinates to be in the nucleus, which we assume has infinite mass. Also, \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) where \( \mathbf{r}_i \) and \( \mathbf{r}_j \) are the vector coordinates of the \( i^{th} \) and \( j^{th} \) electrons and we have written \( X_{N+1} \equiv x_1, x_2, ..., x_{N+1} \) where \( x_i \equiv r_i \sigma_i \). \( Z \) indicates the nuclear charge and \( \mathbf{E}(t) \) is the time-dependent electric field of the light pulse.

In \( R \)-matrix theory [11] the position space occupied by the electrons is divided into two regions. Figure 1 displays the division of many-electron position space which underlies \( R \)-matrix theory. In the inner region (region I), which surrounds the nucleus, a many-electron
wave function is expanded over $R$-matrix eigenstates and many-electron atom-laser Hamiltonian matrix elements are calculated explicitly. In region I all $N + 1$ electrons of the system have a radial co-ordinate $r_q \leq b$, $q = 1, ..., N + 1$. In the outer region (region II) only one electron (or at most two) is present and the electron there, besides experiencing the laser field directly, is aware of the remainder of the atomic system only via long-range multi-pole interactions. Region II is defined by $N$ electrons having a radial coordinate $r_q \leq b$, $q = 1, ..., N$ and one electron having its radial coordinate $r_{N+1} > b$. In the RMT method the time-dependent wavefunction in region II is represented over a finite-difference grid by its values at equidistant grid points $r_{N+1}(i) = ib, i = i_b, i_b + 1, ..., i_R$. Traditionally, $R$-matrix theory is a theory where time is not explicitly involved in the study of the collision or photoionisation processes. However, the potential to employ $R$-matrix theory to solve the TDSE for a multi-electron atom has recently been demonstrated by combining the $R$-matrix theory of scattering with low-order time-propagation techniques [13, 14]. More recently the potential to exploit the powerful $R$-matrix division-of-space concept in order to enable the carry-over of HELIUM code methods to describe multi-electron atomic systems has been set out for the simple one-electron hydrogen atom [12].

In that case, a high-order Taylor propagator was employed and the feasibility of combining basis set methods with finite-difference methods for describing the laser-atom interaction was firmly established. Since then, we have adapted the method to employ the Arnoldi propagator [8, 6] throughout both regions to provide an efficient method for multi-electron systems [9, 10]. We now provide an overview of the RMT method in the outer and inner regions respectively.

2.1. The RMT Outer Region

In region II, the time-dependent $N+1$ electron wave function is expanded as $\Psi(X_{N+1}, t) = \sum_{p} \Phi_{p}^{1} F_{p}(r, t)$, where the $F_{p}$ functions are single-electron functions describing the radial motion of the ejected electron (in the $p$-th channel), and where the radial variable of the $(N + 1)$-th electron is denoted as $r_{N+1} = r$. The $\Phi_{p}$ are channel functions formed by coupling the states of the residual system, $\Phi_{p}(X_{N})$, with angular and spin parts of the ejected electron wave function.

By projecting the known target functions $\Phi_{p}$ onto the TDSE and integrating over all spatial variables except the radial coordinate of the ejected electron, the following set of coupled homogeneous partial differential equations for the radial functions, $F_{p}(r, t)$, is obtained:

$$i \frac{\partial}{\partial t} F_{p}(r, t) = H_{b_{p}}(r) F_{p}(r, t) + \sum_{p'} [W_{E_{pp'}}(r) + W_{D_{pp'}}(t) + W_{P_{pp'}}(r, t)] F_{p'}(r, t) \quad (3)$$

Eq.(3) is the evolution equation for the wave function in region II. In eq.(3), $W_{E}$ is referred to as the long range potential in the $R$-matrix literature and arises from the electron-electron and electron-nuclear potential terms in the Hamiltonian. $W_{D}$ arises from the interaction of the light field with the residual N-electron ion. The $W_{P}$ potential arises from the interaction of the light field with the ejected electron. $H_{b_{p}}$ is the time-independent part of the Hamiltonian in region II. Each of the terms on the right-hand-side of eq.(3) are given explicitly in [9, 10, 13].

To solve the set of coupled partial differential equations given in equation (3) we employ finite difference methods. The radial channel functions $F_{p}(r, t)$ are discretized on an equidistant grid as depicted in figure 1. The second derivative operator in equation (3) is recast in a 5-point finite difference representation. However, the inner boundary of the finite-difference region is not at the nucleus, where $r = 0$, but at some distance from the nucleus at $r = b$. The 5-point finite-difference rule when applied to the radial channel function at the first grid point, $i = i_b$, thus requires information on the value of the radial channel function at points $i = i_b - 1$ and $i = i_b - 2$. (The function value at $i = i_b - 1$ is also needed when the rule is applied to the function at grid point $i = i_b + 1$.) These two grid points lie just inside the outer boundary of the inner region. Since the wavefunction is assumed to be one-electron in nature moving...
outwards from the boundary at \( r = b \), then, so long as \( b \) is chosen large enough, it can also be assumed that the wavefunction has still a one-electron character at the slightly smaller radial distance corresponding to the inner region grid point at \( i = i_b - 2 \) (this can also be enforced). Evaluating the basis expansion coefficients, \( C_k(t) \), at time \( t \) means that the radial wavefunction of the ejected electron at inner-region points \( i = i_b - 1 \) and \( i = i_b - 2 \) can be obtained at time \( t \). The finite-difference Hamiltonian may then be applied to the wavefunction in the outer region.

To propagate the Outer Region wavefunction forward in time, from time \( t \) to time \( t + \delta t \), we employ the Arnoldi propagator [8]; its implementation is similar to that described in [6]. We assume that at time \( t \) the wavefunction is known throughout the inner and outer regions, a valid assumption since the ground state wavefunction will be known initially at \( t = 0 \). At each time step the radial wavefunction of the ejected electron in the inner region at \( r = b - h \) is calculated. This enables the kernel \( H^j \Psi \) operation of the Arnoldi propagator in the outer region to be calculated. We turn now to the propagation of the inner region wavefunction.

2.2. The RMT Inner Region
In region I, the time-dependent \( N+1 \) electron wave function \( \Psi(X_{N+1}, t) \) is represented over an \( R \)-matrix eigenbasis \( \psi_k(X_{N+1}) \) as \( \Psi(X_{N+1}, t) = \sum_k C_k(t)\psi_k(X_{N+1}) \) where \( r_{N+1} \leq b \) and where \( C_k(t) \) are time-dependent coefficients. The TDSE in the inner region is given by eq.(1). However, in region I, the Hamiltonian \( H_{N+1} \) is not Hermitian owing to the presence of the kinetic energy term, \(-\frac{1}{2}\nabla_i^2\), in eq.(2) and the finite value of the wave function on the inner-region boundary. Consequently a Bloch operator \( \mathcal{L}_{N+1} = \frac{1}{2} \sum_{i=1}^{N+1} \delta(r_i - b) \frac{\partial}{\partial r_i} \) is introduced which is such that

\[
H_I(t) = H_{N+1} + \mathcal{L}_{N+1}
\]

is Hermitian in region I. The TDSE in region I may then be written as

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \Psi_I(X_{N+1}, t) = H_I(t) \Psi_I(X_{N+1}, t) - \mathcal{L}_{N+1} \Psi(X_{N+1}, t),
\]

where \( \Psi_I(X_{N+1}, t) \) is the wave function defined over region I in figure 1. By projecting eq. (4) onto the eigenstates \( \psi_k(X_{N+1}) \) we obtain the evolution equations for the coefficients \( C_k(t) \):

\[
\frac{d}{dt} C_k(t) = -i \sum_{k'} H_{I,kk'}(t) C_{k'}(t) + i S_k(t)
\]

where

\[
S_k(t) = \frac{1}{2} \sum_p \omega_{pk} \left. \frac{\partial F_p(r, t)}{\partial r} \right|_{r=b}
\]

and where the \( \omega_{pk} \) are surface amplitudes [11]. At this point it should be emphasized that eq.(5) is fundamental to the RMT method in two ways. Firstly, the inhomogeneous \( S_k \) term on the right-hand-side compensates for the Bloch term introduced to make \( H_I \) Hermitian. Note that it makes a contribution only at \( r = b \) and brings into play there \( \Psi(X_{N+1}, t) \), a wave function form which has been defined throughout both regions. This term is central to any time propagation scheme in region I because it connects the wave function form \( \Psi_I(X_{N+1}, t) \), which is many-electron in nature, with a wave function form that, at \( r = b \), represents a single electron and which, numerically, is obtained from region II. Secondly, eq.(5) allows for two different numerical methods to be brought together, one (basis set) most appropriate to the many-electron finite region I and the other (finite difference) most appropriate to the one-electron region II.

An approximate solution of eq.(5) can be written in terms of so-called \( \phi \) functions [15] as

\[
C(t + \delta t) \approx e^{-i\delta H_I} C(t) + \sum_{j=1}^{n_e} \delta t^j \phi_j(-i\delta H_I) U_j(t),
\]

where
where we have used matrix notation and where
\[ U_0(t) = C(t), \quad U_j(t) = \frac{d^{j-1}}{dt^{j-1}} S(t). \] (8)

The \( \phi_j( -i \delta t H_I ) \) functions are related to the exponentiation of the Hamiltonian matrix, \( H_I \), and are due to the time-dependent inhomogeneity in eq.(5). For a scalar argument \( z \) the \( \phi_j(z) \) functions are defined by the integral representation
\[ \phi_j(z) = \frac{1}{(j-1)!} \int_0^1 e^{(1-\theta)z} \theta^{j-1} d\theta, \quad j \geq 1. \] (9)

For the calculation of the second term on the right-hand-side of eq.(7) an Arnoldi-based method was implemented to calculate the action of the \( \phi_j( -i \delta t H_I ) \) functions on the \( U_j(t) \) functions. The method is similar to that used to calculate the action of \( e^{-i \delta t H_I} \) on \( C(t) \) [9, 10]. In the current implementation of the RMT method, the calculation of the \( \phi_j(z) \) functions is tackled by following an idea set out in [16] and generalised in [17].

The procedure outlined above is repeated for each of the \( \phi_j( -i \delta t H_I ) U_j \) terms in the summation on the right-hand-side of eq.(7). Summing these \( n_t \) terms and adding to the first term on the right-hand-side of eq.(7) then provides us with a means of propagating the wavefunction in the \( R \)-matrix inner region forward one step in time. By this stage the wavefunction is known at time \( t + \delta t \) throughout regions I and II and we can progress further in time by repeating, for successive time steps \( \delta t \), the procedures described in subsection 2.1 and in this subsection.

3. Illustrative results

![Figure 2](image-url)

**Figure 2.** Ionization rates for He (left) and Ne (right) exposed to laser pulses with a central wavelength of 248 nm.

As a means of demonstrating the accuracy of the RMT method, single-electron ionization rates have been calculated for He and Ne irradiated by a laser pulse with a central wavelength of 248 nm (corresponding to the fundamental wavelength of the KrF laser). These rates are compared with rates obtained using the time-independent \( R \)-matrix Floquet (RMF) method and, in the case of He, also with those obtained using the HELIUM code. A detailed description of the atomic structure and the laser field parameters used in these calculations can be found...
in [10]. Figure 2 shows the comparison of the calculated ionization rates for He (left side of figure) and Ne (right side of figure). In the case of He, away from resonances, the ionization rates calculated by RMT agree well (to within 10%) with those calculated by HELIUM [19] and by the RMF method [18]. In the case of Ne, agreement between the RMT results and RMF results is also very good, typically within 10% of each other away from resonance.

4. Conclusion
We have described the development of a powerful new \textit{ab initio} RMT code that has the unique capability to accurately and efficiently describe the single ionization response of a general many-electron atom exposed to intense laser light pulses. The RMT code has immense flexibility since it can not only describe the response of a general many-electron atom to intense laser light fields with wavelengths ranging throughout the spectrum, from the extreme ultraviolet to the infrared, but also to both short- and long-duration pulses of such light. The development of the RMT code has been made possible by implementing the numerical methods and algorithms underlying two well-established \textit{ab initio} methods, namely the methods underlying the HELIUM code [6] and the R-matrix method [11]. We have demonstrated the accuracy of the new RMT method by finding very good agreement between results produced by the RMT method and results produced by HELIUM and the R-matrix Floquet methods. In the near future we intend to adapt the RMT method so as to accurately describe the single-electron ionisation of a multi-electron molecule irradiated by intense short laser pulses. We also see the current method as forming a natural prerequisite for the development of a method that can accurately describe the double-electron ionisation of atoms and molecules exposed to intense short laser pulses.

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