Multi-Configuration Time-Dependent Hartree for Fermions and Bosons

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Methods and Codes for Atoms and Molecules in Strong Laser Fields
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When an IR laser pulse hits an atom...

Electron density of the Hydrogen atom
2-cycle pulse
2 \times 10^{14} \text{ W/cm}^2
800\text{nm}

Dramatic, non-perturbative dynamics
Very large volume covered
Very complex structure (seemingly)
Characteristics of our systems

Laser electric field \sim \text{atomic field strength} \\
=> (highly) non-perturbative \\
=> large simulation volumes

Short \text{time scales}: 150 \text{attoseconds} \sim \text{electron orbit time} \\
=> non-stationary, wave-packet like situation

Several electrons are involved: \\
-- Auger process \\
-- strong field ionization \\
-- re-scattering \\
-- molecules

Both, \text{continuous and bound}, parts of the system \\
=> both, quantum and near classical, behavior
Why are infrared strong field simulations difficult?

### Size of the problem
Scaling with intensity \( I \) and wave-length \( \lambda \)

<table>
<thead>
<tr>
<th>Description</th>
<th>Scaling</th>
<th>Numbers (*)</th>
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<tbody>
<tr>
<td>Quiver energies:</td>
<td>( \sim I \times \lambda^2 )</td>
<td>(~ 12 \text{ eV} )</td>
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</tr>
<tr>
<td>Grid spacing for drift momenta:</td>
<td>( \sim I^{1/2} \times \lambda )</td>
<td>(~ 1 \text{ Bohr} )</td>
</tr>
<tr>
<td>Box size = pulse duration \times \text{drift momentum}</td>
<td>( \sim I^{1/2} \times \lambda^2 )</td>
<td>(~ 500 \text{ Bohr} )</td>
</tr>
</tbody>
</table>

Grid points / dimension: \( \sim I \times \lambda^3 \) \ (~ 500)

(*) 5 cycle pulse, intensity \( 2 \times 10^{14} \text{W/cm}^2 \), wave length \( 800 \text{ nm} \)

### Total grid points

1 electron  \# of dimension = 2: \( 500^2 = 250000 \) grid points \(~ I \times \lambda^4 \)

2 electrons  \# of dimensions = 5: \( 500^5 = 3 \times 10^{13} \) grid points \(~ I^{5/2} \times \lambda^{10} \)
Why few-electron dynamics is hard...

The quantum wave function $\Psi$
(contains everything we can know about the system)

$$\Psi(x_1,y_1,z_1,x_2,y_2,z_2,\ldots,x_n,y_n,z_n)$$  

$n$...number of electrons

Exponential growth of information with $n$
(good for quantum computing, bad for real computing)

Much more information than we ever want to know

Represent only part of that information:

Time-dependent density functional theory (TDDFT)
  – never generate $\Psi$, use only single particle density

Time-dependent Hartree-Fock (TDHF)
  – assume $\Psi$ is an (anti-symmetrized) product of single particle functions
(Time-dependent) Hartree-Fock method – TDHF

Approximate the electron wave function by a product of strongly inter-dependent three-dimensional orbitals

\[ \Psi(r_1,r_2,...,r_n;t) = \det[\Phi_1(r_1;t) \Phi_2(r_2;t) ... \Phi_n(r_n;t)] \]

Orbitals \( \Phi \) are optimal for each time \( t \)
We hope/assume that the determinant ansatz is suitable
+ compact representation of the wave function (some 10 MB)
+ straight forward extraction of experimental observables
- large computational effort (much larger than TDDFT)
- no checks of accuracy
- fails for strong time-dependent interactions

Time-dependent density functional theory - TDDFT
suffers from similar problems, possibly more severely
Why time-dependent Hartree-Fock fails

A two-electron system in various states

Initial state (a configuration)

Partial ionization

Ionized state (another configuration)

Another state (more configurations)

Yet another state....

Symbolic representation

Quantum wave

\[ \Psi(r_1, r_2) \approx A_{ab} \Phi_a(r_1) \Phi_b(r_2) + A_{cd} \Phi_c(r_1) \Phi_d(r_2) + A_{ef} \Phi_e(r_1) \Phi_f(r_2) + \ldots \]
MCTDH F&B

Multi-Configuration Time-dependent Hartree for Fermions and Bosons

**Hartree:** Few-particle wave function \( \approx \) Product of single particle wave function

\[
\Psi(x_1, \ldots, x_f) \approx \phi_1(x_1)\phi_2(x_2) \ldots \phi_f(x_f)
\]

**Multi-Configuration:** use linear combination of products

\[
\Psi(x_1, \ldots, x_f) \approx \sum_{j_1=1}^{n} \ldots \sum_{j_f=1}^{n} A_{j_1,...,j_f} \phi_{j_1}(x_1)\phi_{j_2}(x_2) \ldots \phi_{j_f}(x_f)
\]

**Time-dependent:** single-particle functions \( \phi_j(x, t) \) and linear coefficients \( A_{j_1,...,j_f}(t) \) depend on time

**Fermions / Bosons:** restrict to anti-symmetric / symmetric

\[
A_{\ldots j_k \ldots j_\mu \ldots} = \pm A_{\ldots j_\mu \ldots j_k \ldots}
\]
MCTDHF

\[ \Psi(r_1, \ldots, r_n; t) = \sum_{j_1=1}^{M} \sum_{j_2=1}^{M} \cdots \sum_{j_n=1}^{M} A_{j_1 \ldots j_n}(t) \det[\Phi_{j_1}(r_1, t) \Phi_{j_2}(r_2, t) \ldots \Phi_{j_n}(r_n, t)] \]

Orbitals \( \Phi \) are optimal for each time \( t \) ("basis moves with the solution")

There is no bias in the ansatz (except for finite \( M > n \))

+ compact representation of the wave function (~ 100 MB)
+ straightforward extraction of experimental observables
+ exact in the limit of many configurations

- somewhat larger computational effort than TDHF
- complexity like a quantum chemistry code (much higher than TDHF)
- non-linear time-evolution equations
Why can one gain by MCTDHF&B?

Correlated $\Psi(x,y;t)$ approximated by products $\Phi_j(x;t)\Phi_k(y;t)$

$\Phi_j(x;t)$ and $\Phi_k(x;t)$ evolve with the system

Compact representation of $\Psi(x,y;t)$

Price to pay: non-linear equations of motion
Variational optimality of the solution

**Dirac-Frenkel variational principle:**

\[ \langle \delta \Psi | H - i \partial_t | \Psi \rangle = 0 \]

*Time-locally optimal* solution (not necessarily globally optimal)

**Variations – compatible with multi-conf. Hartree structure**

\[ \delta \Psi = \frac{\delta \Psi}{\delta \phi_i} \delta \phi_i + \frac{\delta \Psi}{\delta A_{j_1...j_f}} \delta A_{j_1...j_f} \]

**Non-uniqueness of the ansatz**

Any invertible matrix \( S \)

\[ \Psi \text{ invariant under:} \]

\[ \phi_j \rightarrow \sum_i S_{ji} \phi_i \]

\[ A_{j_1...j_f} \rightarrow \sum_{l_1...l_f} A_{l_1...l_f} (S^{-1})_{l_1j_1} \cdots (S^{-1})_{l_f j_f} \]

→ “Gauge” freedom
Dynamical equations

System of non-linear PDEs

\[ i \frac{d}{dt} A_{l_1 \ldots l_f}(t) = \sum_{l_1 \ldots l_f} \langle \phi_{j_1} \ldots \phi_{j_f} | H(t) - G^{(1)}(t) | \phi_{l_1} \ldots \phi_{l_f} \rangle A_{l_1 \ldots l_f} \]

\[ i \frac{d}{dt} \phi_j = G^{(1)}(t) + P_\perp[\Phi] \sum_{l,m=1}^{n} \langle P_\perp[\Phi] \rangle^{-1} \langle (H - G)[A, \Phi] \rangle_{lm} \phi_m \]

“Gauge” \[ G^{(1)}(t) = \sum_{i=1}^{f} G(x_i, t) \]

Problem size (system dependent):
- Number of orbitals \( n \sim 10 \)
- Length of vector \( A \) \( \sim 10^3 \)
- Grid size for \( r \) \( 10^4 \sim 10^5 \)

Main cost: evaluation at each time step of
\[ \langle \Phi_{j_1} \ldots \Phi_{j_n} | H | \Phi_{k_1} \ldots \Phi_{k_n} \rangle \text{ and } \langle H - G[A(t), \Phi(t)] \rangle \]

Note: the limit \( n \to \infty \) recovers the exact TDSE
Individual terms in the equations...

\[ i \frac{d}{dt} \phi_j = G^{(1)}(t) + \sum_{l,m=1}^{n} \left( \rho[A] \right)_{jl} \left( \langle H - G \rangle [A, \phi] \right)_{lm} \phi_m \]

Projector on space orthogonal to \( \Phi \)'s

\[ P_\perp = 1 - \sum_{n=1}^{N} |\phi_n\rangle \langle \phi_n| \]

Single particle reduced density matrix

\[ \rho_{jl} = \sum_{j_2 \ldots j_f} A^*_{j_j \ldots j_f} A_{j_2 \ldots j_f} \]

Mean field operator (for \( G=0 \))

\[ \hat{H}_{mn} = \frac{(f-1)(f-2)}{2} \sum_{m_2n_2} \langle \phi_{m_2} | H | \phi_{n_2} \rangle \rho^{(2)}_{m_2n_2,mn} \]

Hamiltonian with two-particle interactions

\[ H = \sum_{k=1} \sum_{k<n} H(x_k, x_n, t) \]

Two-particle reduced density matrix

\[ \rho^{(2)}_{j_1j_2l_1l_2} = \sum_{j_3 \ldots j_f} A^*_{j_1j_2j_3 \ldots j_f} A_{l_1l_2j_3 \ldots j_f} \]
Literature on MCTDHF&B

M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer:
“The multiconfiguration time-dependent Hartree method:
A highly efficient algorithm for propagating wavepackets.”

J. Caillat, J Zanghellini, M. Kitzler, W. Kreuzer, O. Koch, A. Scrinzi:
"Correlated Multielectron Systems in Strong Laser Pulses
- An MCTDHF Approach";

“Multidimensional Quantum Dynamics: MCTDH Theory and Applications”
(Wiley, 2009)
Very high accuracies needed – high order methods preferred
### Convergence of the He ground state energy

<table>
<thead>
<tr>
<th>Number of orbitals</th>
<th>L=0</th>
<th>L=1</th>
<th>L=2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.86168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-2.87898</td>
<td></td>
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<tr>
<td>12</td>
<td></td>
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<td>-2.9009</td>
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<tr>
<td>15</td>
<td></td>
<td>-2.9004</td>
<td>-2.9019</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td>-2.9021</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td>-2.9023</td>
</tr>
</tbody>
</table>

∞ (Literature) | -2.9005 | -2.9027

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95% of the correlation energy

Exacting explicitly correlated basis


-2.90372437703411959382

Max. single-particle ang. momentum

Literature: explicitly correlated basis

Exact: explicitly correlated basis


-2.90372437703411959382

95% of the correlation energy
**Ionization of He, Li, Be**

Ionisation yield for a single-cycle 800 nm pulse

**Ionisation potential**
- He 24.6 eV
- Li 5.4 eV
- Be 9.3 eV

**Intensity relative to intensity at 50%**

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity, W/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$3.5 \times 10^{15}$</td>
</tr>
<tr>
<td>Be</td>
<td>$8.6 \times 10^{13}$</td>
</tr>
<tr>
<td>Li</td>
<td>$1.2 \times 10^{12}$</td>
</tr>
</tbody>
</table>
Limitations of the method

"Double-ionization" (1d model)

Time-dependent HF
MCTHDF (15 and 45 configurations)
TDSE (same spatial discretization)

\[
V_\eta = -\frac{2}{\sqrt{1 + x_1^2}} - \frac{2}{\sqrt{1 + x_2^2}}
\]

\[
V_{12} = \frac{1}{\sqrt{1 + (x_1 - x_2)^2}}
\]

Two-particle density \(|\Psi(x_1, x_2)|^2\)
Computational questions

**Discretization:**
- differential and multiplication operators

**Electron interaction:**
- non-local with respect to single orbitals $\Phi(r)$
- very large operations count

**Parallelization:**
- reduce band-width requirements
- load balancing

**Time-propagation:**
- non-linear equations
- expensive evaluation of derivatives

**General use and long term development:**
- portability
- maintenance

**Our solution**
- local discretizations
- FEM, DVR, finite differences

- low-rank approximations
- H-matrix techniques

- low-rank approximation
- run-time load balancing

- high order Runge-Kutta
- partial exponentiations
  (unsatisfactory)

- extensive use of abstract types
- standard F90/F95
Example: the multi-configuration wave function type

Strict modularization =>

Public/private variables =>

Extensive use of derived types =>

MCTDHF wave function =>

Module contains all methods for its type =>

```
module m_mchwf
  use m_finite_element
  use m_coordinate_axis
  use m_orbital

  public :: mchwf ! type: mchf wave function
  public :: mchwf_write ! write to file
  public :: mchwf_natural ! transform to natural orbitals
  public :: mchwf_mpi_unite ! unite on master

  type mchwf ! a complete mchwf wave functions plus a few parameters
    complex(size), pointer :: a(:) ! A - coefficients
    type (orbital), pointer :: o(:) ! Phi - orbitals
    logical :: restricted=.false. ! restricted/unrestricted HF
    character(size) :: gauge='none' ! 'length','velocity'
    real(size) :: time=0.0 ! Psi(x,t)
    type(multi_index_space), pointer :: s ! multi-index (Fermions/Bosons)
    real(size) :: ener=0.0,apot=0.0 ! energy,vector potential
  contains
    subroutine mchwf_write(s,what,fb,a,message)
      ! write a mchf wave function to a file
      ! what ... 'first','append'='next'),'overwrite'
      ! file ... definition of the output file
      ! a ... the mctdhf wave function
      character(*) :: what
    end subroutine mchwf_write
  end type mchwf

end module m_mchwf
```

Emulate C++ in Fortran... ;-)
Spatial discretization

Product bases in 3-dimensional single particle space

for a range of coordinate systems (cartesian, polar, cylindrical,...)

Discretization on each coordinate

- High-order finite elements with variable grids in each dimension
  (good for parallelization, high order for rapid convergence)
- FE-DVR (special FE with a Lobatto quadrature)
- Special eigenbases (trigonometric, spherical harmonics)
- Numerical eigenbases (e.g. of parts of the hamiltonian)

Discretization points (problem dependent): \( n \sim \text{from } 10 \text{ to } 10^5 \)
Two-particle interactions

Write $V_{12}(r_i - r_j)$ as a sum of products

\[
V_{12}(|\vec{r}_i - \vec{r}_j|) \approx \sum_{m=1}^{M} U_m(\vec{r}_i) W_m(\vec{r}_j)
\]

After discretization: low-rank approximation for a matrix
(a) truncate a Schmidt-decomposition or
(b) hierarchical (H-)matrix technique

e.g. Coulomb multipole expansion for large separations
H-matrix – performance + flexibility

Two-body interaction is most expensive...
~ matrix of dimension $2n \times 2n \sim 10^5 \times 10^5$ application at EACH TIME STEP
n...single-particle discretization

Hierarchical (H-) matrices

Performance
n log n method (cf. FFT, “fast multipole”)

Flexibility
“Automatically” adjusts to different interactions
(Coulomb, $\delta(x-x_0)$, screened,...)

Parallelization
Sub-blocks are better localized
Solving the Dynamical Equations

Heterogeneous components – different time scales in $H^{(1)}$ and $H^{(2)}$

**Separation of time-scales by “preconditioning”**

Choose the “gauge” $G^{(1)}$ to generate much of the dynamics of $\varphi$

- e.g. $G^{(1)} = H^{(1)}(t_0)$ with $t_0$ within the current time step

Write equations in terms of

\[
\chi_j(\mathbf{x}, t) = U(t, t') \phi_j(\mathbf{x}, t')
\]

\[
i \frac{d}{dt} U(t, t') = G^{(1)}(t) U(t, t')
\]

(solve by methods for linear systems, “cheap”)

“Expensive” two-particle equations

\[
i \frac{d}{dt} \chi_j = UP_{\perp}[U^{-1}\chi] \sum_{l,m=1}^{n} (\rho(A))^{-1}_l \langle (H - G^{(1)})(A, U^{-1}\chi) \rangle_{lm} U^{-1}\chi_m
\]

solve with large step sizes / high order methods
Parallel inversion the finite-element overlap matrix

Overlap of disconnected finite elements
\( S_0 \) (inversion perfectly parallel)

Continuity conditions imposed
\( S \)

Related by projection
\[ QS_0 Q = S \]

Generalization of the Woodbury formula

Inverse:
\[ S^{-1} = QS_0^{-1} Q - QS_0^{-1} P (P S_0^{-1} P)^{-1} P S_0^{-1} Q \]

\[ [P = 1 - Q] \]

Applying projectors \( P \) and \( Q \) requires very little communication
Parallelization

- Scatter orbitals over cpu's
- Calculation of mean fields: non-local interaction reduced by low-rank approximation
- Application of mean fields: strictly local
- Differential operators have negligible communication

Dynamic load balancing: balance CPU load during computations
Dynamic load balancing

Measure the CPU load during run-time
If imbalance, move boundaries between CPUs (binary search)

Load pattern changes slowly during the run
Negligible overhead after initial phase
Significant real time gains

~ 40% gain

Numbers: elements on CPU

<table>
<thead>
<tr>
<th>Step</th>
<th>CPU1</th>
<th>CPU2</th>
<th>CPU3</th>
<th>CPU4</th>
<th>CPU5</th>
<th>CPU6</th>
<th>CPU7</th>
<th>CPU8</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8</td>
<td>8</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>7</td>
<td>8</td>
<td>8</td>
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</table>
Electron density of a molecule in an IR field

Ideal absorbing boundary
no reflections from box boundary

Reduce the simulation volume
to the necessary minimum
(e.g. \( r < R \sim 20 \) a.u.)

WITHOUT any change
to the wave function inside \( r < R \)

Exterior complex scaling
does exactly that
with moderate numerical effort

Simulation in a large (but finite) box

-2.6
-1.3
0
1.3
2.6

Time (femtoseconds)

Nice!
First garbage
Complete garbage

X
50
-50
Why are infrared strong field simulations difficult?

**Size of the problem**

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<td>$\sim I^{1/2} \times \lambda^2$</td>
<td>$\sim 500$ Bohr</td>
</tr>
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| Grid points / dimension: | $\sim I \times \lambda^3$ | $\sim 500$ |

(*) 5 cycle pulse, intensity $2 \times 10^{14}$ W/cm$^2$, wavelength 800 nm

**Total grid points**

- 1 electron # of dimension = 2: $500^2 = 250000$ grid points $\sim I \times \lambda^4$
- 2 electrons # of dimensions = 5: $500^5 = 3 \times 10^{13}$ grid points $\sim I^{5/2} \times \lambda^{10}$

**BUT**

Relevant physics on length scale $\sim$ a few Bohr!
Everything outside is boring (almost free motion)

Why simulate outside part on a huge computer??
Are we wasting factors $500^5$?
**Complex scaling of the Hamiltonian**

Use complex factor $e^{i\theta} \cdot r \rightarrow e^{i\theta} r$

$$H = -\frac{1}{2}\Delta - V(r^*) \quad \rightarrow \quad H_\theta = -\frac{e^{-2i\theta}}{2}\Delta - V(r^*e^{-i\theta}) \quad \theta \in \mathcal{R}$$

Note: $H_\theta$ is non-hermitean

Note: $V(r)$ should be an analytic function!? 
General properties of complex scaling

Family of analytic continuations $H_\theta$ of a Hamiltonian $H = H_{\theta=0}$

1. All $H_\theta$ have same bound state spectrum as $H_{\theta=0}$
2. $H_\theta$ have additional complex $L^2$ eigenstates -> resonances
3. for $\theta > 0$, $H_\theta$ have continuous spectrum in the lower complex plane
4. projectors on bound eigenstates are analytic functions of $\theta$
5. matrix elements of the resolvent $(H_\theta - E)^{-1}$ are analytic functions of $\theta$
Non-analytic $V(r)$: exterior complex scaling

We can relate complex scaling to outgoing wave boundary conditions

$\Rightarrow$ only long-range behavior matters

Hamiltonian is **analytic only beyond** $R_0$

complex scale only beyond a finite distance $R_0$

\[ r \rightarrow r \quad \text{for} \quad r < R_0 \]
\[ r \rightarrow R_0 + e^{i\theta} (r-R_0) \quad \text{for} \quad r > R_0 \]
What can we compute by complex scaling?

**Stationary problems**

- Complex scaled energies \( E + i\Gamma/2 \)
  - Resonance position \( E \)
  - Resonance with \( \Gamma \)
- Matrix elements of the resolvent
- Bound-continuum dipole matrix elements

**Time-dependent problems**

- Population of resonances / doubly excited states by short pulses
- Time-dependent wave function in a finite region
- High harmonic spectra
- IR photo-electron spectra from a TDSE calculation
Implementation of exterior complex scaling

Important technical complications
Bra and ket functions are not from the same space!!!

Exterior scaled Laplacian $\Delta_{R_0, \Theta}$ is defined on discontinuous functions

$$\Psi(R_0 - 0) = e^{3i\theta/2} \Psi(R_0 + 0)$$

Discontinuity arises because we need to keep the norm constant
Discontinuity is reversed for the left hand functions

$$\Psi^*(R_0 - 0) = (e^{-3i\theta/2} \Psi)^*(R_0 + 0)$$

Matrix elements of $\Delta_{R_0, \Theta}$
are computed by piece-wise integration $[0, R_0] + [R_0, \infty)$

Conditions easy to implement with a local basis set
Discretization: high order finite elements

Finite elements = piecewise polynomials

Special feature: “infinite elements” at the ends with $p_n(x) \exp(-\alpha x)$

“irECS” – infinite range Exterior Complex Scaling

Example:
4 elements, order=3

In practice:
Order 10 ~ 40
20 ~ 8 elements

Total of ~ 200 points
Why do we gain by complex scaling?

If we do not need the asymptotic information in $\Psi$, we do not need to compute it!

E.g. a resonant state

Replace by exponential tail

I.e. compute a smooth compact function in a small box instead of a wiggly function in a large box
The complex scaled wave function $\Psi_\theta$ has no direct physical meaning.

**Back-scaling**

$$\Psi(\vec{r}, t) = \text{Backscale}[\Psi_\theta(\vec{r})] = \Psi_\theta(e^{-i\theta \vec{r}})$$

Is it mathematically justified?

No prove - numerical evidence will be presented.

**Can we in practice retrieve the asymptotic information?**

Obviously not completely – it is just what we have thrown away.

E.g. outgoing waves become exponentially damped in space and time.
Exterior complex scaling for the TDSE

Solve

\[ i \frac{d}{dt} \Psi_{\theta R_0}(x, t) = H_{\theta R_0}(t) \Psi_{\theta R_0}(x, t) \]

Hope that

\[ \Psi_{\theta R_0}(x) = \Psi(x) \quad \text{for } |x| < R_0 \]
Does it work?

Atom in a strong dipole field

\[ i \frac{d}{dt} \Psi(x, t) = \left[ -\frac{1}{2} \Delta_x + i \vec{A}(t) \cdot \vec{\nabla}_x + V(x) \right] \Psi(x, t) \]

Pulse parameters: \(2 \times 10^{14} \text{ W/cm}^2\), 760 nm, 5 opt. cycl. FWHM

**Massive ionization:**
At the end of the pulse \(~80\%\) of the probability is outside \([-40,40]\)

Accuracy of the solution (1-dimensional)

Relative error

\[ \frac{|\Psi_{\theta R_0}(x) - \Psi(x)|}{|\Psi_{\theta R_0}(x) + \Psi(x)|} \]

Inside box \(~10^{-7}\)

Works very nicely!

[Phys. Rev. A81, 53845 (2010)]
irECS is a perfect absorber

Errors are determined by the accuracy of the discretization
Mathematically speaking there are NO errors introduced by ECS itself
How many discretization points are needed?

Error measure: \( \| \Psi_{\theta R_0} (x) - \Psi(x) \|^2_{x < R_0} / \| \Psi(x) \|^2_{x < R_0} \)

Points in unscaled region 160

Points for absorption

\( M_A = 10 \)

\( M_A = 20 \)

20 Absorption points are perfect!

Quite insensitive to scaling angle \( \theta \) and exponential \( \exp(-\alpha x) \)

[Phys. Rev. A81, 53845 (2010)]
## Compare to complex absorbing potentials (CAPs)

Errors of ECS and CAPs with identical discretizations

<table>
<thead>
<tr>
<th>Method</th>
<th>$M_A$</th>
<th>$A$</th>
<th>$\theta$ or $\sigma$</th>
<th>$q$</th>
<th>$\mathcal{E}[{-R_0, R_0}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>irECS</td>
<td>21</td>
<td>$\infty$</td>
<td>0.6</td>
<td></td>
<td>$2 \times 10^{-15}$</td>
</tr>
<tr>
<td>ECS</td>
<td>20</td>
<td>10</td>
<td>0.6</td>
<td></td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>ECS</td>
<td>40</td>
<td>20</td>
<td>0.5</td>
<td></td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>CAP</td>
<td>20</td>
<td>10</td>
<td>$10^{-4}$</td>
<td>4</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>CAP</td>
<td>20</td>
<td>10</td>
<td>$2 \times 10^{-6}$</td>
<td>6</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>CAP</td>
<td>40</td>
<td>20</td>
<td>$4 \times 10^{-6}$</td>
<td>4</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>CAP</td>
<td>60</td>
<td>30</td>
<td>$6 \times 10^{-7}$</td>
<td>4</td>
<td>$1 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

*Number of points* | *Accuracy*

[Phys. Rev. A81, 53845 (2010)]
What else is important?

**High order**

Error relative to unscaled calculation with same order

\[
\begin{array}{cccc}
\text{p}_n, n \neq 1, N & \text{p}_1 & R_0 & \epsilon[-35, 35] \\
4 & 41 & 40 & 4 \times 10^{-8} \\
5 & 41 & 40 & 1 \times 10^{-7} \\
6 & 41 & 40 & 3 \times 10^{-10} \\
7 & 43 & 39 & 1 \times 10^{-9} \\
9 & 41 & 40 & 5 \times 10^{-12} \\
11 & 41 & 40 & 9 \times 10^{-12} \\
13 & 37 & 42 & 2 \times 10^{-13} \\
15 & 46 & 38 & 7 \times 10^{-14} \\
21 & 41 & 40 & 2 \times 10^{-15}
\end{array}
\]

**IrECS**

Infinite end elements

\[
\begin{array}{cccc}
A & M_A & \epsilon[-40, 40] \\
\infty & 21 & 2 \times 10^{-15} \\
20 & 20 & 4 \times 10^{-4} \\
40 & 40 & 2 \times 10^{-11} \\
60 & 60 & 1 \times 10^{-9} \\
80 & 80 & 1 \times 10^{-15}
\end{array}
\]

**Correct implementation of derivatives**

Basis must be **discontinuous** at \( R_0 \)

Leads to **non-positive** mass-matrix (= overlap-matrix)
Observation:
Wave function is not just absorbed in the scaled region
It returns from the exterior scaled region without distortions

~ 1% probability returns
from scaled region |x| > 5
into unscaled region |x| < 5

Wave-function in |x| < 5
accuracy < \(10^{-11}\) at all times

Dynamics is correctly encoded also in the scaled region!

Yes, we can hope... in practice: neither easy nor very important
In 3 dimensions

Works just the same way and equally robust and efficient
Perfect high harmonic responses for H and model Ne
Very stable wave functions when varying scaling parameters $R_0$ and $\theta$

High harmonic spectrum of the Hydrogen atom

![High harmonic spectrum graph](image-url)
Electrons are absorbed **before the pulse is over!**

Modifications of electron energies after absorption! → match to Volkov solutions at some cutoff-radius $R_c$

Values and derivatives

\[ Real \; \Psi(R_c), \; \Psi'(R_c) \equiv \psi_\Theta(R_c), \; \psi'_\Theta(R_c) \] complex scaled for $R_c < R_0$

**Photoelectron spectrum (1d)**

Pulse $2 \times 10^{14}$ W/cm$^2$, 760nm, 1cycle

Unscaled with box [-600,600]
Scaled with box [-30,30]

Scaled is
More than 100 times faster!
More accurate!
Short range potential
use $R = 10$

$$U_{ef}(r) = \begin{cases} e^2 \left[ \frac{1}{r} + \frac{r^2}{(2R^3)} - \frac{3}{(2R)} \right] & \text{for } r \leq R \\ 0, & \text{for } r > R. \end{cases}$$

Laser: 3 cycles, $1 \times 10^{14}$ W/cm²

**NO dependence on $R_c = 15, 25, 35$ Bohr**

![Graphs showing electron spectra for different values of $R_c$]
**Photoelectron spectra – 3d (Coulomb)**

**Coulomb - 2 additional problems:**

1. Volkov solutions are inaccurate for Coulomb before $R_c \sim 50$
2. Bound states extend to very large distances

**Solution**

1. solve the scattering problem outside $r \sim 20$ (easy)
2. remove bound states before calculating surface values

... not fully implemented yet

**Dependence on $R_c = 28, 38, 48$ Bohr**

- **Partial Wave $l=0$**
  - $\lambda=760\text{nm}$, 1 optical cycle
  - $I=1 \times 10^4 \text{W/cm}^2$
  - $Pulse \text{ duration } 1 \text{ opt.cycl}$

- **Partial Wave $l=2$**
  - $\lambda=760\text{nm}$, 3 optical cycles
  - $I=1 \times 10^4 \text{W/cm}^2$
  - $Pulse \text{ duration } 3 \text{ opt.cycl}$

**Methods and codes in strong fields**
Dubling, April 27-30, 2011, p. 48
MCTDHF:
  capture moderate correlation
  (like CASSCF/MCHF)

Key code properties:
  flexible discretization: FEM, bases
  all numerical quadratures
  → fully flexible potentials (coulomb, delta-like, harmonic...)
  e-e interaction – H-matrices
  parallel
  “Object oriented” coding (F95!)

Absorption:
  very promising solution by irECS
Technical details

• Particle numbers: up to 8 ~ 12

• 1-particle discretization:
  product bases, FEM, DVR; $10^5 \sim 10^6$ linear coefficients

• General 1-particle coordinates (cylinder, polar, cartesian, …)

• General 1-particle potentials (full precision numerical quadratures)

• General 2-particle operators: H(=hierarchical)-matrix technique

• MPI-parallel: scales up to ~ 30 CPUs (not fundamental limitation)

• Run-times: ~ hours (parallel)

• Also for few-boson systems
The procedure: real scaling of the Hamiltonian

**Real scaled Hamiltonian**

\[ H_\lambda = U^*(\lambda) H U(\lambda) \]

Unitary transformation leaves the spectrum invariant

**Real scaled Hydrogen atom**

\[ H = -\frac{1}{2}\Delta - \frac{1}{r} \quad \rightarrow \quad H_\lambda = -\frac{e^{-2\lambda}}{2}\Delta - \frac{e^{-\lambda}}{r} \]

Note: different factors at kinetic and potential energies

**Real scaled Helium atom**

\[ -\frac{1}{2}\Delta_1 - \frac{2}{r_1} - \frac{1}{2}\Delta_2 - \frac{2}{r_2} + \frac{1}{r_{12}} \quad \rightarrow \quad -\frac{e^{-2\lambda}}{2}\Delta_1 - \frac{2e^{-\lambda}}{r_1} - \frac{e^{-2\lambda}}{2}\Delta_2 - \frac{2e^{-\lambda}}{r_2} + \frac{e^{-\lambda}}{r_{12}} \]
Real scaling of the coordinates

Change the units of length

\[ \Psi(\vec{r}) \rightarrow \Psi_\lambda(\vec{r}) = e^{3\lambda/2} \Psi(e^\lambda \vec{r}) \quad \lambda \in \mathcal{R} \]

Scalar product of scaled functions

\[ \langle \Phi_\lambda | \Psi_\lambda \rangle = \int_{\mathcal{R}^3} d\vec{r} \Phi^*_\lambda(\vec{r}) \Psi_\lambda(\vec{r}) \]

note normalization!

\[ = \int_{\mathcal{R}^3} d\vec{r} e^{3\lambda} \Phi^*(e^\lambda \vec{r}) \Psi(e^\lambda \vec{r}) = \langle \Phi | \Psi \rangle \]

Unitary transformation

\[ \Psi_\lambda = U(\lambda) \Psi \quad U^*(\lambda)U(\lambda) = 1 \]
Resonances – shape resonance

A toy potential for resonances

![Graph showing a toy potential for resonances](image)
Doubly excited states – Feshbach resonances

**Hamiltonian of He:** \( H^{(1)}(r_1) + H^{(1)}(r_2) + H^{(2)}(r_1 - r_2) \)

**He\(^+\): Spectrum of \( H^{(1)}(r_1) \)**

**Spectrum of \( H^{(1)}(r_1) + H^{(1)}(r_2) \)**

all product states: \(|1>|1>, |1>|2>, ... |2>|k>, ..., |3>|k>,.....

**Spectrum of \( H^{(1)}(r_1) + H^{(1)}(r_2) + H^{(2)}(r_1 - r_2) \)**

Bound states with admixtures of continuum
Time-dependent problems: static field ionization

Decay of Hydrogen in a static field

\[ i \frac{d}{dt} \Psi_\theta(\vec{r}, t) = \left[ -\frac{e^{-2i\theta}}{2} \Delta - \frac{e^{-i\theta}}{r} + e^{i\theta} \vec{E} \cdot \vec{r} \right] \Psi_\theta(\vec{r}, t) \]

\[ \Psi_\theta(\vec{r}, t = 0) = \Phi_{0,\theta}(\vec{r}) \]

Overlap with the ground state

\[ \left| \langle \Phi_{0,\theta}^* | \Psi_\theta(\vec{r}, t) \rangle \right|^2 \]

Extra conjugation \( \Phi_{0,\theta}^* \)
Resonances – structure in the continuum

Phase-shifts of the scattering states

asymptotics \( \psi_k(r) \sim e^{ikr} + e^{-i[kr+\varphi(k)]} \)

\( \varphi(k) \) (rapidly) changes by \( \pi \)

Density of states

has a (sharp) peak near the resonance energy

Complex poles of the scattering matrix \( S(k) \)

Analytically continue \( S(k) \)
find poles in the complex plane
(near the real axis)

Complex scaling

Analytically continue the Hamiltonian to a non-hermitian operator
find complex eigenvalues of the Hamiltonian
(near the real axis)
What do we mean by outgoing wave boundary conditions?

Write $\Psi(r;t)$ in terms of scattering states asymptotics: $\Phi_k(r) \sim e^{ikr}$
(bounds states omitted for simplicity)

Schrödinger equation for $c(k;t)$

$$i\frac{d}{dt} c(k;t) = \int_{-\infty}^{\infty} dk' h(k,k';t)c(k';t)$$

Keep only outgoing $\Phi_k(r) : k>0$

$$i\frac{d}{dt} c^+(k;t) = \int_{0}^{\infty} dk' h(k,k';t)c^+(k';t)$$

Outgoing wave solution

$$\Psi^+(r;t) = \int_{0}^{\infty} dk' c^+(k';t)\Phi_k(r)$$
Complex scaling for in- and outgoing waves
(Advanced handwaving 2)

Complex scaled TDSE

\[ i \frac{d}{dt} \Psi(\eta r; t) = H(\eta r; t) \Psi(\eta r; t) \]

Assume plenty of analyticity

Complex scaled \( \Psi \) in terms of complex scaled scattering states \( \Phi_k(\eta r) \)

\[ \Psi(\eta r; t) = \int_{-\infty}^{\infty} dk \ c_\eta(k,t) \Phi_k(\eta r) \]

\( \Psi \) and \( \Phi_k \) analytic \( \implies \) \( c_\eta \) independent of \( \eta \)

\[ c_\eta(k,t) \equiv c(k,t) \]

Real and complex scaled TDSE describe the same dynamics

Asymptotics (\( \text{Im} \ \eta > 0 \))

\[ \Phi_k(k\eta r) \sim e^{ik\eta r} = e^{ik \Re c(\eta)r} \times e^{-k \Im m(\eta)r} \]

Complex scaled ingoing \( (k<0) \) waves diverge exponentially
Complex scaling = outgoing wave boundary conditions
(Advanced handwaving 3)

Solve the complex scaled TDSE in the space of normalizable functions

=> all ingoing wave content of $\Psi$ is suppressed

In the complex scaled TDSE
in- and out-going waves are distinguished
by normalizibility

(1) Normalizibility is easier to impose than asymptotic conditions
(2) Scaling is needed only asymptotically
Example: Resonance (double excited state) of $\text{H}_2$

Potential energy curves for $\text{H}_2$ (bound and continuous states) [F. Martin & group]
(simulation with a very large box)

Doubly excited states

Strictly speaking, doubly excited “states” are continuous states
=> hard to represent

Still, they are “states” with nearly discrete and $L^2$ character

Complex scaling describes doubly excited states on their natural length scale
Literature (very incomplete)

Mathematics and mathematical physics (1970's)
Balslev, Aguillar, Combes: Proofs and mathematical foundations
Barry Simon: “exterior” complex scaling

Quantum chemistry (from 1980's)
Junker, Reinhardt, Moiyseev: methods& implementations
Many more applications...

Physics (from the 1970s)
Rescigno, McCurdy, A.S.: systems in strong fields
Putz et al.: quantum dots in bias fields

Mostly applied to time-independent systems...

Time-dependent
A.S., Piraux, 1998: nice results for He in UV pulses
He et al., 2007, Tao et al. 2009: ~ does not really work for IR fields (?)
How to compute

**Coulombic systems**

Choose a (real) basis $|i\rangle$

Matrix representations of kinetic and potential energies

$$\hat{T}_{ij} = \langle i | T | j \rangle \quad \hat{V}_{ij} = \langle i | V | j \rangle$$

Matrix representations of Hamiltonian

$$\hat{H}_{ij} = \langle i | T + V | j \rangle = \langle i | T | j \rangle + \langle i | V | j \rangle$$

Matrix representations of complex scaled Hamiltonian

$$\hat{H}_\theta = e^{-2i\theta} \hat{T} + e^{-i\theta} \hat{V}$$

**Non-coulomb systems**

must compute $\hat{V}_{\theta,ij} = \langle i | V(e^{i\theta} r) | j \rangle$

Note: $V(r)$ should be an analytic function!?