The accurate numerical solution of the Schrödinger equation with an explicitly time-dependent Hamiltonian

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A reference . . .

This talk is based on

V. Ledoux, M. Van Daele

Solving the time-dependent Schrödinger problem using the CP approach

Computer Physics Communications **185** (2014) 1589-1594.

Sturm-Liouville problems

MATSLISE is a Matlab package for solving Sturm-Liouville and Schrodinger equations

It has been developed by Veerle Ledoux under the supervision of Guido Vanden Berghe and VD in a close collaboration with Liviu Ixaru (Bucharest).

V. Ledoux, VD Matslise 2.0, a Matlab toolbox for Sturm-Liouville computations, Transactions on Mathematical Software, **22** 4 (2016) article 29.

Sturm-Liouville problems

Find an eigenvalue E and corresponding eigenfunction $y(x)$ $\not\equiv 0$ such that

$$-(p(x)y'(x))' + q(x)y(x) = Ew(x)y(x)$$

with boundary conditions

$$a_1 y(a) + a_2 p(a) y'(a) = 0, \quad b_1 y(b) + b_2 p(b) y'(b) = 0,$$

where $|a_1| + |a_2| \neq 0 \neq |b_1| + |b_2|$.

Schrödinger equation : special case whereby $p = w = 1$

$$y'' + q(x)\, y = E\, y$$

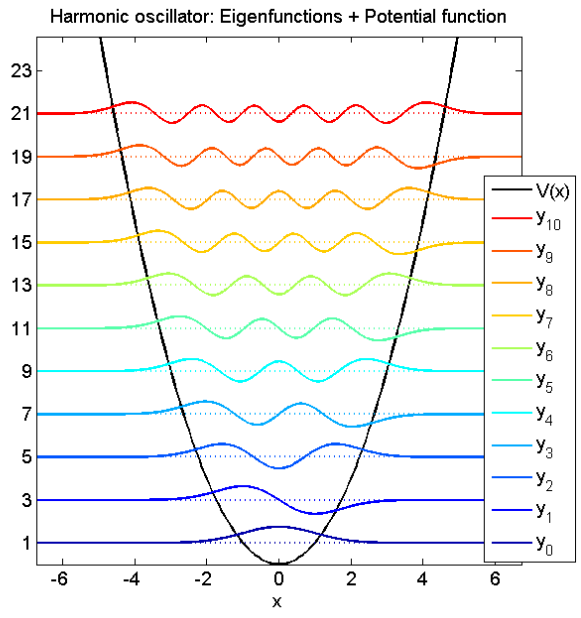
Regular Sturm-Liouville problems

The eigenvalues of a regular SLP can be ordered as an increasing sequence tending to infinity

$$E_0 < E_1 < E_2 < \dots$$

E_k has index k.

The corresponding $y_k(x)$ has exactly k zeros on the open interval (a, b).

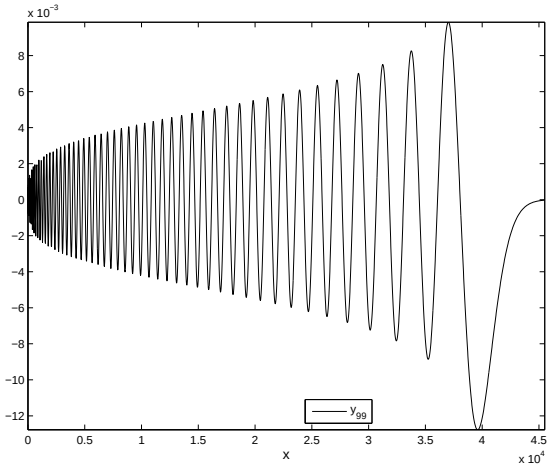


Distinct eigenfunctions are orthogonal with respect to $w(x)$

$$\int_a^b y_i(x) y_j(x) w(x) dx = 0, \quad i \neq j.$$

How to solve Sturm-Liouville problems

Problem: as the index k increases, the corresponding y_k become increasingly oscillatory.



Standard numerical methods for ODEs encounter difficulties in efficiently estimating the higher eigenvalues.

Naive integrators will be forced to take increasingly smaller steps, thereby rendering them exceedingly expensive.

Example : the Paine problem

$$-y'' + \exp(x)\, y = E\, y \qquad y(0) = y(\pi) = 0$$

The errors ($\times 10^3$) obtained with the Numerov algorithm, the Numerov method with correction technique and the EF-Numerov scheme.

k	E_k	$10^3\,(E_k - \tilde{E}_k)$	$10^3\,(E_k - \tilde{E}_{CT,k})$	$10^3\,(E_k - E_{EF,k})$
0	4.8966694	0.0028	0.0027	0.0014
2	16.019267	0.2272	0.1114	0.0424
4	32.263707	2.8802	0.3879	0.1959
6	56.181594	19.687	0.8159	0.4535
8	88.132119	87.276	1.4108	0.8115
10	128.10502	290.92	2.1961	1.2859
12	176.08900	797.57	3.2082	1.9073
14	232.07881	1898.8	4.5015	2.6947
16	296.07196	4063.9	6.1589	3.7168
18	368.06713	8000.6	8.3076	5.0273

How to solve Sturm-Liouville problems

Taking into account the characteristic features of the SL problem, one can construct specialized numerical algorithms having some crucial advantages over general-purpose codes.

Some early (seventies to nineties) codes on SL problems :

- SLEIGN (Bailey et al.)
- SLEDGE (Fulton-Pruess)
- SL02F (Marletta-Pryce)
- SLCPM12 (Ixaru-Vanden Berghe-De Meyer)

MATSLISE originates from SLCPM12 .

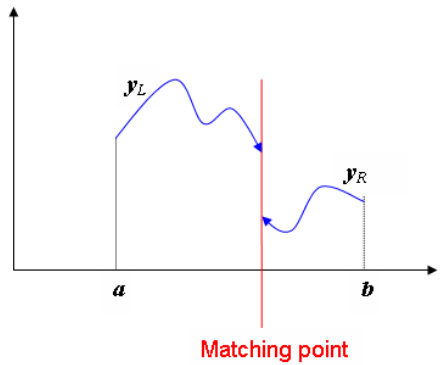
In the next slides we focus on the special techniques used in MATSLISE .

Basic ideas: 1. Shooting

Shooting methods transform the boundary value problem into an initial value problem.

One solves the differential equation for a succession of trial values of E which are adjusted till the boundary conditions at both ends can be satisfied at once, at which point we have an eigenvalue.

The simplest technique is to shoot from a to b, but multiple shooting is preferred.



The eigenvalues are the solutions of a mismatch function $\phi(E)$:

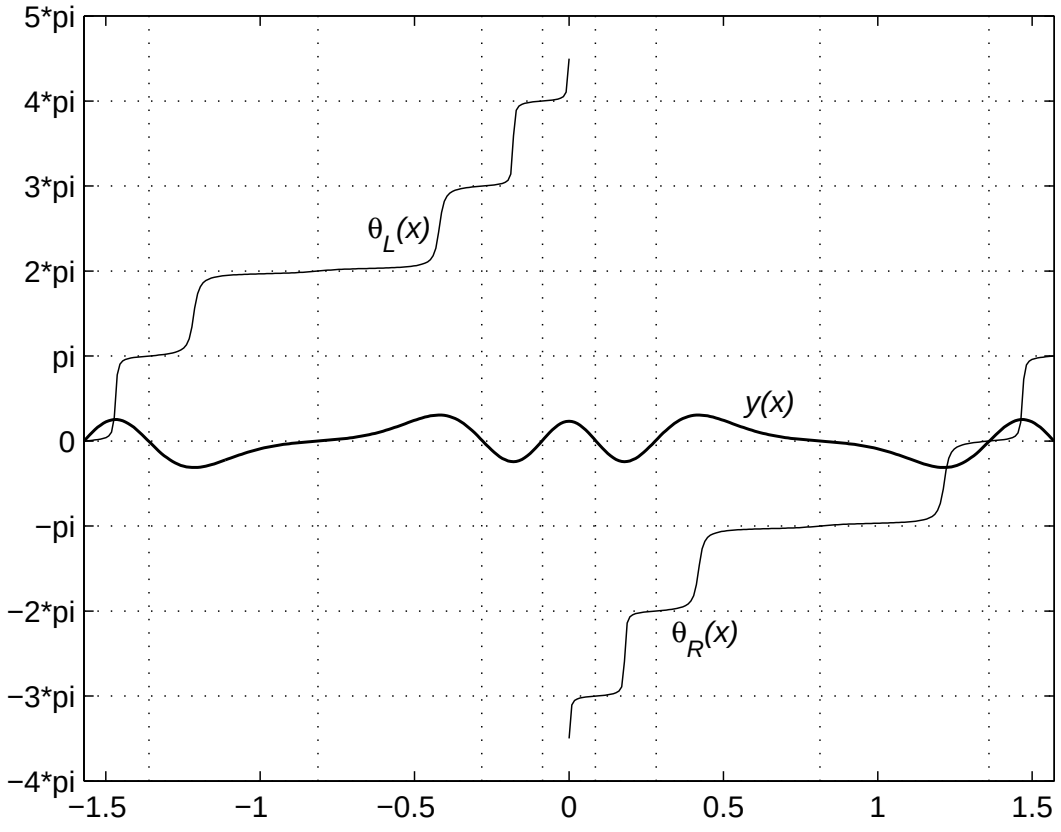
$$\phi(E) = y_L(x_m, E)p(x_m)y'_R(x_m, E) - y_R(x_m, E)p(x_m)y'_L(x_m, E).$$

Basic ideas: 2. Prüfer transformation

Suppose we have found an eigenvalue : $\phi(E) = 0$.

What is its index?

Solution: use the (scaled) Prüfer transformation.



Basic Ideas: 3. Coefficient Approximation

Idea behind second order Pruess method:

Let $a = x_0 < x_1 < x_2 < \cdots < x_n = b$ be a partition of $[a, b]$.

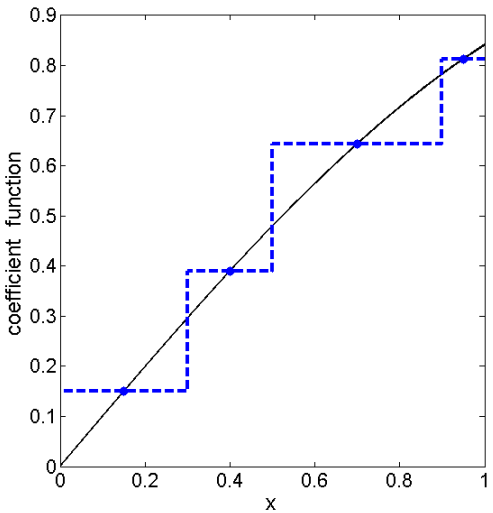
Replace

$$-(p(x)y'(x))'+q(x)y(x) = Ew(x)y(x)$$

in the interval (x_{i-1}, x_i), $i = 1, \ldots, n$ by

$$-(\bar{p}y'(x))' + \bar{q}y(x) = E\bar{w}y(x).$$

where $\bar{p}$, $\bar{q}$, $\bar{w}$ are constant.



Basic Ideas: 4. Perturbation theory

Higher order methods are obtained by expressing the solution as a series and by adding correction terms to the second order method.

All terms in this series can be computed analytically if the coefficient functions are polynomials.

Therefor, we first approximate the coefficient functions by polynomials of degree N

CPM[N,Q] : Convergence results

for problems that are reformulated in Schrödinger form ...

Let N be the degree of the polynomial approximating $q(x)$ and let Q be the number of correction terms. The corresponding CPM method is denoted is CPM[N,Q].

L.Gr. Ixaru, H. De Meyer and G. Vanden Berghe, CP methods for the Schrödinger equation, revisited, *J. Comput. Appl. Math.* **88** (1997) 289–314.

The error in the eigenvalue E_k, obtained with CPM[N,Q],

- is of order $\mathcal{O}(h^{2N+2})$ for small E if $Q \geq \lfloor \frac{2}{3}N \rfloor + 1$
- is of order $\mathcal{O}(h^{2N})/\sqrt{E}$ for large E if $Q \geq \delta_{N0}$

Time-dependent Schrödinger equation

$$\imath \frac{\partial \psi(x,t)}{\partial t} = \hat{H}(x,t)\psi(x,t), \quad x \in \mathbb{R},\ t > 0$$

with the one-dimensional time-dependent Hamiltonian

$$\hat{H}(x,t) = -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + V(x,t),$$

initial data $\psi(x,0) = \psi_0(x)$

μ is the reduced mass

units are chosen such that $\hbar = 1$

Standard techniques

Standard techniques lead to the linear system

$$\imath \frac{d}{dt} Z(t) = H(t) Z(t)$$

$$Z = (Z_1, \ldots, Z_N)^T$$

H: $N \times N$ hermitian matrix

Standard technique 1

Discretisation of the spatial variable x

Define $\psi(x_j, t) = Z_j(t)$, $j = 1, \ldots, N$

$$\imath \frac{d}{dt} Z_j(t) = -\frac{1}{2\mu} \frac{Z_{j+1}(t) - 2\, Z_j(t) + Z_{j-1}(t)}{\Delta x^2} + V(x_j, t)$$

Standard technique 2

Spectral decomposition of $\psi(x,t)$:

$$\psi(x,t) = \sum_{m=1}^{N} Z_m(t)\, y_m(x)$$

whereby $\{y_m(x) | m \in \mathbb{N}\}$ is an orthonormal basis
(of eigenfunctions of some time-independent Hamiltonian)

E.C. Titchmarsh

Eigenfunction expansions associated with second order differential equations

Oxford University Press, Oxford, 1962.

Our approach: sector-dependent expansion

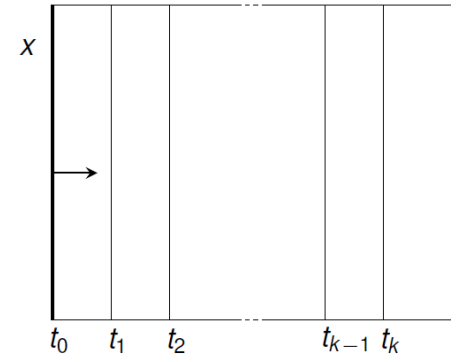
We use an idea by L.Gr. Ixaru:

L.Gr. Ixaru, New Numerical method for the eigenvalue problem of the 2D Schrödinger equation

Computer Physics Communications **181** (2010) 1738-1742.

$$x \in [x_{\min}, x_{\max}]$$

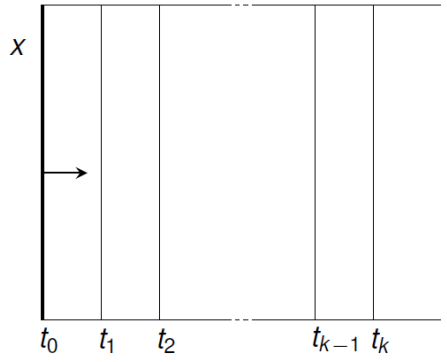
$$t \in [0, T]$$



Inspired by Ixaru, $[0, T]$ is divided into sectors.

Our approach: sector-dependent expansion

Sector k : $t \in [t_{k-1}, t_k]$



In sector k we approximate $V(x,t)$ by $\bar{V}^{[k]}(x)$, such that

$$\hat{H}(x,t) = -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + V(x,t)$$

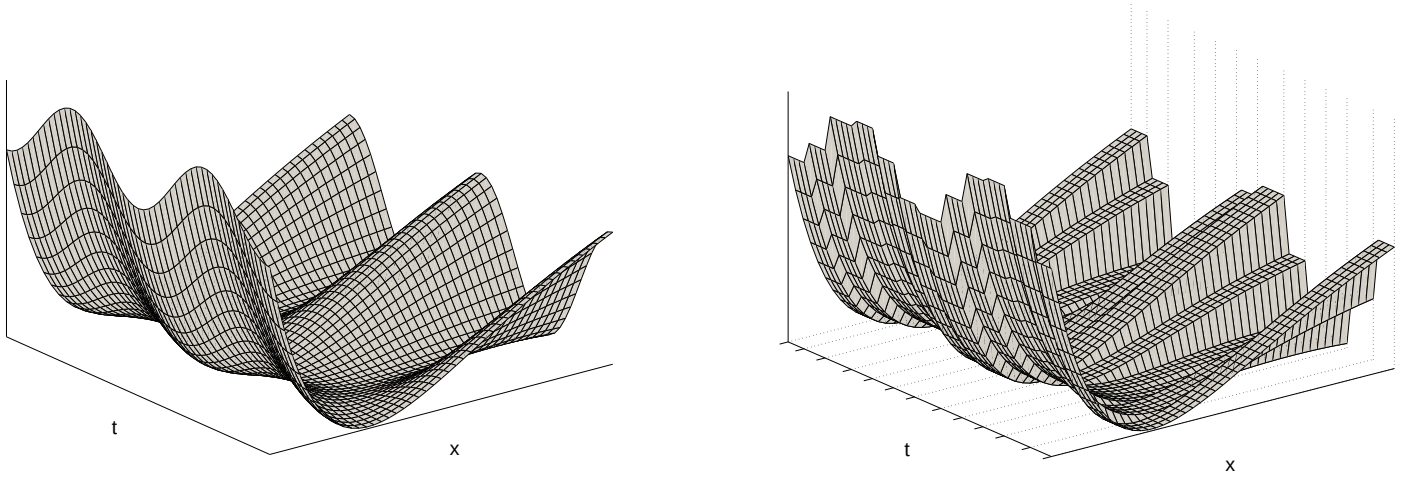
is approximated by

$$\hat{H}^{[k]}(x) = -\frac{1}{2\mu}\frac{d^2}{dx^2} + \bar{V}^{[k]}(x)$$

Sectorwise approximation of $V(x,t)$

In $[t_{k-1}, t_k]$ we approximate $V(x,t)$ by

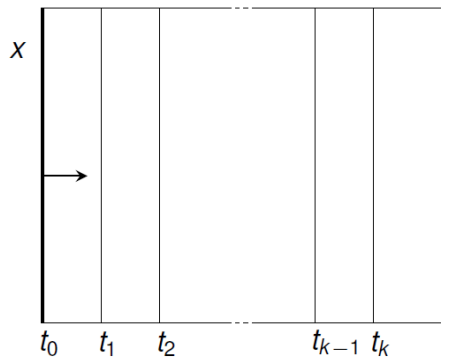
$$\bar{V}^{[k]}(x) = V(x, (t_{k-1} + t_k)/2)$$



$V(x,t)$ and $\bar{V}(x,t)$

Propagation of the solution over one sector

Assume $\psi(x, t_{k-1})$ is known



In $[t_{k-1}, t_k]$ we approximate the solution $\psi(x, t)$ of the TDSE by

$$\psi^{[k]}(x, t) = \sum_{m=1}^{N} c_m^{[k]}(t) y_m^{[k]}(x)$$

Step 1 : choice of $\{y_m^{[k]}(x)|m \in \mathbb{N}\}$

Let $\{y_m^{[k]}(x)|m \in \mathbb{N}\}$ be

the set of orthogonal eigenfunctions of $\hat{H}^{[k]}(x)$.

This requires the solution of the TISE

$$\hat{H}^{[k]}(x)y_m^{[k]}(x) = E_m^{[k]}y_m^{[k]}(x)$$

Step 2: Computation of $c_m^{[k]}(t)$

Substitute $\psi^{[k]}(x,t) = \sum_{m=1}^{\infty} c_m^{[k]}(t) y_m^{[k]}(x)$

in the TDSE $\imath \frac{\partial \psi(x,t)}{\partial t} = \hat{H}(x,t)\psi(x,t)\,.$

$$\imath \frac{d}{dt} c_n^{[k]}(t) = \sum_{m=1}^{\infty} \left[\Delta V_{nm}^{[k]}(t) + E_m^{[k]} \delta_{nm} \right] c_m^{[k]}(t), \quad n = 1, 2, 3, \ldots$$

$$\Delta V_{nm}^{[k]}(t) = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) \left[V(x,t) - \bar{V}^{[k]}(x) \right] y_m^{[k]}(x) \mathrm{d}x$$

Step 2: Computation of $c_m^{[k]}(t)$

Initial values are obtained imposing continuity at t_{k-1}:

$$\psi^{[k-1]}(x, t_{k-1}) = \psi^{[k]}(x, t_{k-1})$$

$$\sum_{m=1}^{\infty} c_m^{[k-1]}(t_{k-1}) y_m^{[k-1]}(x) = \sum_{m=1}^{\infty} c_m^{[k]}(t_{k-1}) y_m^{[k]}(x).$$

Multiply by $y_n^{[k]}(x)$, integrate over x,

and use orthonormality in the r.h.s. to obtain

$$c_n^{[k]}(t_{k-1}) = \sum_{m=1}^{\infty} s_{nm}^{[k]} c_m^{[k-1]}(t_{k-1}) \qquad s_{nm}^{[k]} = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) y_m^{[k-1]}(x) \mathrm{d}x$$

Conclusion: to solve the TDSE in $[t_{k-1}, t_k]$

1. solve the TISE $\hat{H}^{[k]}(x)y^{[k]}(x) = E^{[k]}y^{[k]}(x)$
2. compute integrals

$$s_{nm}^{[k]} = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) y_m^{[k-1]}(x) \mathrm{d}x$$

$$\Delta V_{nm}^{[k]}(t) = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) \left[V(x,t) - \bar{V}^{[k]}(x) \right] y_m^{[k]}(x) \mathrm{d}x$$

3. solve a linear system $C^{[k]\prime}(t) = A^{[k]}(t)C^{[k]}(t)$

initial conditions : $C^{[k]}(t_{k-1}) = S^{[k]}C^{[k-1]}(t_{k-1})$

$$A_{nm}^{[k]}(t) = -\imath \left[\Delta V_{nm}^{[k]}(t) + E_n^{[k]}\delta_{nm} \right]$$

1. Solution TISE

In order to have

- a computationially efficient approximation technique for the solution of the TISE,
- and to obtain a uniform high accuracy approximation to the eigenvalues and eigenfunctions

we use Constant Perbutation methods as in MATSLISE).

Here we use CP methods with a predefined uniform mesh (in order to minimize the number of CP eigenfunction evaluations).

2. Computation of the integrals

Instead of using standard quadrature rules for integrands with a highly oscillatory or exponential character

we use so-called exponentially-fitted quadrature rules especially adapted to this particular problem:

the CP approach does not only provide us with the values of the wavefunctions at the meshpoints but also those of their first derivative.

Ixaru L. Gr. Ixaru, and G. Vanden Berghe,
Exponential Fitting, Kluwer, 2004.

Computation of $s_{nm}^{[k]} = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) y_m^{[k-1]}(x) \mathrm{d}x$

Suppose one approximates

$$y''(x) = 2\,\mu(V(x) - E)\,y(x)$$

by

$$\bar{y}''(x) = 2\,\mu(\bar{V} - E)\bar{y}(x)\,.$$

Since

$$\bar{y}(x) = f_1 \exp(2\,\mu\sqrt{\bar{V} - E}x) + f_2 \exp(-2\,\mu\sqrt{\bar{V} - E}x)$$

one may expect

$$y(x) = f_1(x) \exp(2\,\mu\sqrt{\bar{V} - E}x) + f_2(x) \exp(-2\,\mu\sqrt{\bar{V} - E}x)\,.$$

Computation of $s_{nm}^{[k]} = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) y_m^{[k-1]}(x) \mathrm{d}x$

If

$$\begin{aligned} y_n^{[k]}(x) &= f_1(x)\exp(\omega_n^{[k]}x) + f_2(x)\exp(-\omega_n^{[k]}x) \\ y_m^{[k-1]}(x) &= g_1(x)\exp(\omega_m^{[k-1]}x) + g_2(x)\exp(-\omega_m^{[k-1]}x) \end{aligned}$$

then

$$\begin{aligned} y_n^{[k]}(x) y_m^{[k-1]}(x) &= h_1(x)\exp(\mu_1 x) + h_2(x)\exp(-\mu_1 x) \\ &\quad + h_3(x)\exp(\mu_2 x) + h_4(x)\exp(-\mu_2 x) \end{aligned}$$

$$\mu_1 = \omega_n^{[k]} + \omega_m^{[k-1]} \text{ and } \mu_2 = \omega_n^{[k]} - \omega_m^{[k-1]}$$

Computation of $s_{nm}^{[k]} = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) y_m^{[k-1]}(x) \mathrm{d}x$

We choose to use a 4-point Lobatto-EF algorithm of the form

$$\int_{X-h}^{X+h} I(x)\mathrm{d}x \approx h \sum_{n=1}^{4} a_n^{(0)} I(X + x_n h) + h^2 \sum_{n=1}^{4} a_n^{(1)} I'(X + x_n h)$$

which is exact for the functions

$$\exp(\pm\mu_1 x), \exp(\pm\mu_2 x), x\exp(\pm\mu_1 x), x\exp(\pm\mu_2 x)\,.$$

Computation of

$$\Delta V_{nm}^{[k]}(t) = \int_{x_{min}}^{x_{max}} y_n^{[k]}(x) \left[V(x,t) - \bar{V}^{[k]}(x) \right] y_m^{[k]}(x) \mathrm{d}x$$

If $V(x,t)$ is explicitly known and the first derivative w.r.t. x of $V(x,t) - \bar{V}^{[k]}(x)$ can be evaluated, then the same rule can be applied.

If this is not the case, then we use a Lobatto-type rule

$$\int_{X-h}^{X+h} I(x)\mathrm{d}x \approx h \sum_{n=1}^{4} a_n^{(0)} I(X + x_n h)$$

which is exact for the functions

$$\exp(\pm\mu_1 x), \exp(\pm\mu_2 x)\,.$$

3. Solving linear system of ODEs

$$C^{[k]\prime}(t) = A^{[k]}(t)C^{[k]}(t) \qquad A^{[k]}_{nm}(t) = -\imath\left[\Delta V^{[k]}_{nm}(t) + E^{[k]}_{n}\delta_{nm}\right]$$

initial conditions : $C^{[k]}(t_{k-1}) = S^{[k]}C^{[k-1]}(t_{k-1})$

Idea : use coefficient approximation

To obtain a second order method:

replace $A^{[k]}(t)$ in $[t_{k-1}, t_k]$ by $\bar{A}^{[k]} = A^{[k]}((t_{k-1} + t_k)/2)$.

In that case $\bar{A}^{[k]}$ is diagonal such that

$$C^{[k]}(t) = \exp[(t - t_{k-1})\bar{A}^{[k]}]C^{[k]}(t_{k-1}), \quad t \in [t_{k-1}, t_k].$$

3. Solving linear system of ODEs

To obtain higher order methods, we use similar techniques as in MATSLISE (perturbation theory and approximation of the coefficient functions by polynomials)

$$C^{[k]}(t) = DT^D(t - t_{k-1})D^T C^{[k]}(t_{k-1})$$

with

$$T^D(\delta) = \exp(\delta A_0^D) + P_1(\delta) + P_2(\delta) + ...$$

This is equivalent to using modified Neumann integral series.

We have used a fourth order method with

$$T^D(\delta) = \exp(\delta A_0^D) + P_1(\delta)$$

3. Solving linear system of ODEs

We use this fourth order scheme and applied it

- once over the full sector-length $[t_k, t_{k+1}]$ or
- (if needed to ensure accuracy) on a subdivision of the sector $[t_k, t_{k+1}]$.

3. Solving linear system of ODEs

Remark:

Only second order method is unitary, such that the norm is preserved over time.

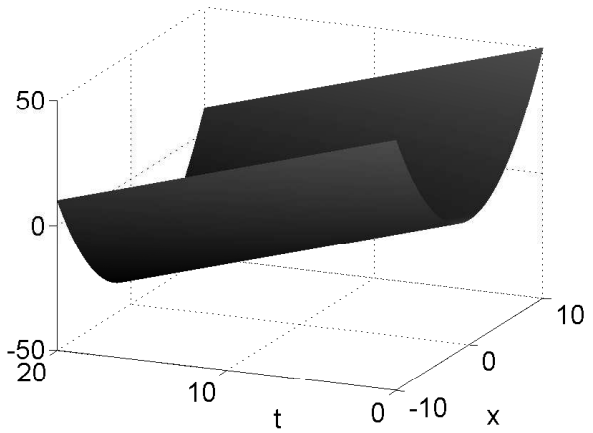
For the higher order methods, this is not the case. But: the correction terms are small and loss of norm conservation is consequently also likely to be small.

Example 1

$V(x,t) = x^2/2 - 2t$

$x \in [-10,10]$, $t \in [0,T] = [0,20]$

$\mu = 1$



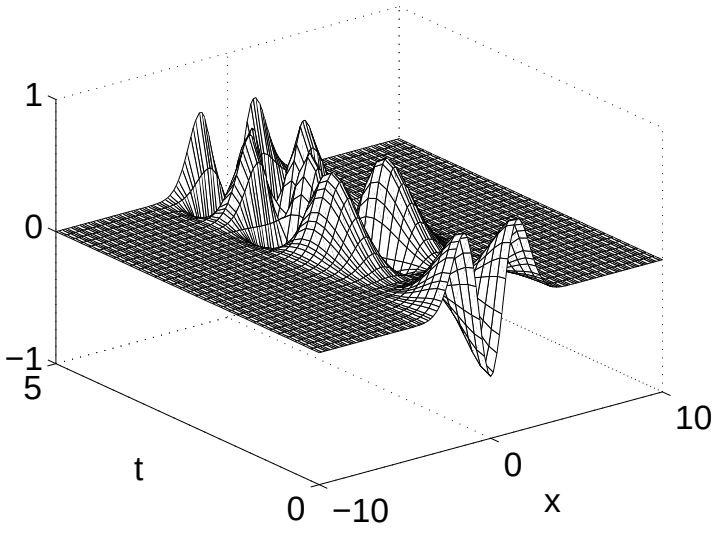
$$\psi(x,0) = (2^n n!\sqrt{\pi})^{-1/2} \exp(-x^2/2) H_n(x)$$

H_n:Hermite polynomial of degree n

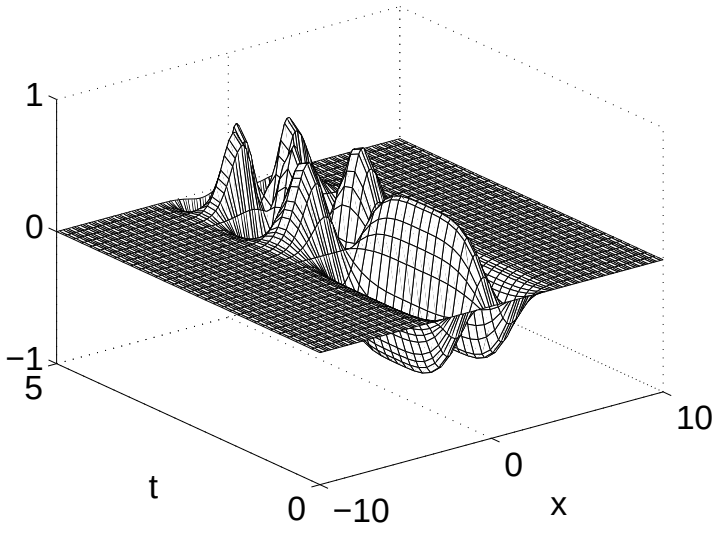
$$\psi(x,t) = \psi(x,0) \exp(-\imath(n+\tfrac{1}{2})t + \imath t^2)$$

Example 1: $t \in [0, 5]$

$\mathcal{R}e\,\psi(x,t)$



$\mathcal{I}m\,\psi(x,t)$

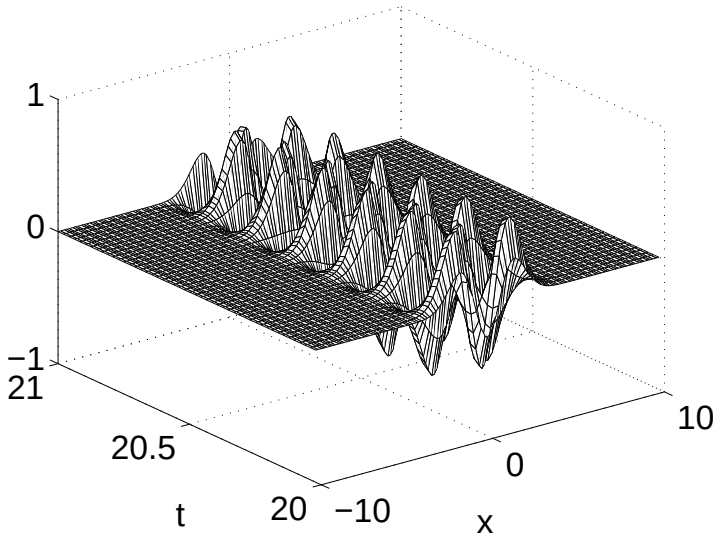


$$\Delta_x = 0.5, \Delta_t = 0.25, N = 12$$

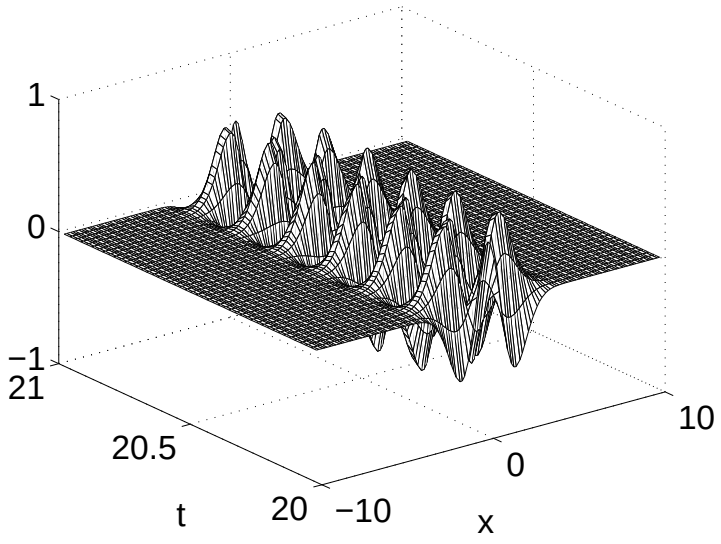
$$n = 2$$

Example 1: $t \in [20, 21]$

$\mathcal{R}e\,\psi(x,t)$



$\mathcal{I}m\,\psi(x,t)$



$$\Delta_x = 0.5, \Delta_t = 0.25, N = 12$$

$$n = 2$$

Error

$$err_N = \int_{x_{min}}^{x_{max}} \psi^{[K]}(x,T)\psi^{*[K]}(x,T)\mathrm{d}x - \int_{x_{min}}^{x_{max}} \psi_{exact}(x,T)\psi^{*}_{exact}(x,T)\mathrm{d}x$$

$$err_A = \max_{x \in \mathrm{mesh}_x} |\psi(x,T) - \psi_{exact}(x,T)|$$

Example 1

		$N = 10, K = 10, T = 20$			$N = 12, K = 5, T = 20$		
	Δ_x	1	0.5	0.25	1	0.5	0.25
	Δ_t	1	1	1	1	1	1
err_N	$n = 2$	7e-5	1e-10	8e-15	6e-5	6e-11	4e-14
	$n = 4$	1e-3	3e-10	2e-14	7e-4	1e-10	1e-14
	$n = 6$	1e-3	5e-10	2e-14	9e-4	2e-10	6e-14
err_A	$n = 2$	1e-4	5e-11	7e-14	5e-4	6e-11	5e-14
	$n = 4$	5e-4	1e-10	6e-14	5e-4	2e-10	7e-14
	$n = 6$	8e-4	1e-10	3e-14	6e-4	1e-10	5e-14
cputime (sec)		6	11	18	4	8	14

Example 1

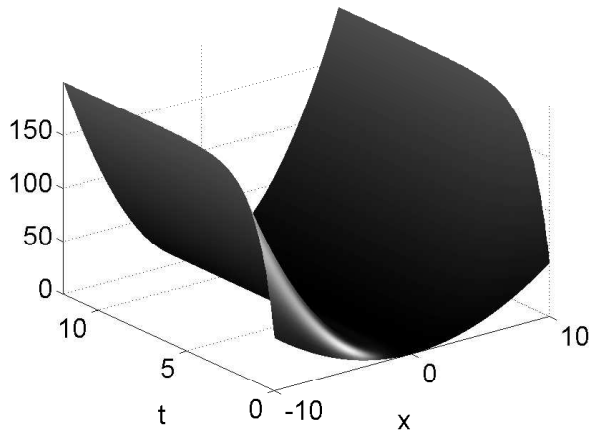
Crank-Nicholson		$T = 2$		$T = 5$
	Δ_x	0.02	0.01	0.02
	Δ_t	0.02	0.01	0.02
err_N	$n = 2$	4e-4	1e-4	5e-3
	$n = 4$	2e-3	5e-4	1e-3
	$n = 6$	4e-3	9e-4	3e-3
err_A	$n = 2$	3e-4	8e-5	8e-3
	$n = 4$	1	1	1
	$n = 6$	8e-1	8e-1	6e-1
cputime (sec)		174	2450	410

Example 2

$$V(x,t) = (4 - 3\,\exp(-t))\,x^2/2$$

$$x \in [-10,10],\ t \in [0,T] = [0,12]$$

$$\mu = 1$$



$$\psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} \exp(-\frac{1}{2}(x-\sqrt{2})^2)$$

Example 2

	$N = 10, K = 20$			$N = 15, K = 20$			
Δ_x	1	0.5	0.25	1	0.5	0.25	0.2
Δ_t	0.6	0.3	0.05	0.6	0.3	0.05	0.02
$\lvert err_N \rvert$	2e-3	5e-5	3e-9	2e-3	5e-5	6e-9	6e-11
err_A	3e-3	8e-5	1e-5	3e-3	8e-5	3e-7	3e-7
time	10	24	62	17	36	104	258

	$N = 20, K = 20$		
Δ_x	0.5	0.25	0.2
Δ_t	0.3	0.05	0.02
$\lvert err_N \rvert$	6e-6	6e-9	6e-11
err_A	8e-5	6e-8	2e-9
time	55	184	390

Example 2

$\Delta_x = 0.2$ and $\Delta_t = 0.02$

N	$K = 1$	$K = 10$	$K = 20$
5	1e-2	3e-3	2e-3
10	3e-4	3e-5	9e-6
15	2e-5	3e-6	3e-7
20	7e-7	4e-8	2e-9
30	2e-9	3e-11	1e-12

Example 3

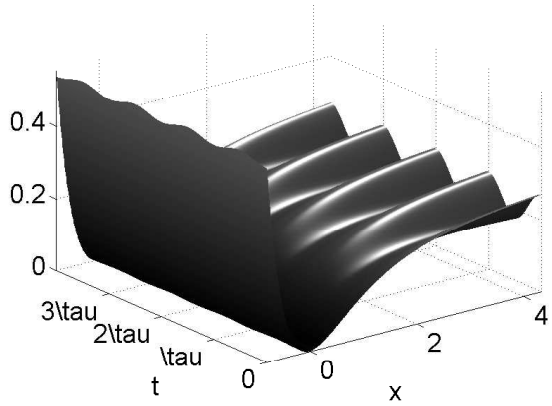
diatomic molecule in strong laser field (Walker and Preston)

$$V(x,t) = D(1-e^{-\alpha x})^2 + A\cos(\omega t)x$$

$$x \in [-1, 4.32]$$

$$t \in [0, 100\tau] \quad \tau = 2\pi/\omega$$

$$\omega = 0.01787$$



$$\psi(x,0) = \psi_0(x) = \sigma \exp(-(\rho - 1/2)\alpha x) \exp(-\rho e^{-\alpha x})$$

$$\mu = 1745 \; D = 0.2251 \; \alpha = 1.1741 \; A = 0.011025 \text{ (a.u.)}$$

$$\rho = 2D/\omega_0, \; \omega_0 = \alpha\sqrt{2D/\mu} \text{ and } \sigma = 0.2411580885 \times 10^{-10}$$

Example 3

$$\Delta_x = \frac{x_{\max} - x_{\min}}{64} \qquad N = 15 \qquad K = 20$$

Δ_t	$\tau/10$	$\tau/20$	$\tau/50$	$\tau/100$	$\tau/200$	$\tau/400$
$\lvert err_N \rvert$	3e-3	1e-4	1e-6	2e-9	5e-10	5e-10
err_A	1e-2	7e-4	2e-5	1e-6	8e-8	5e-9
time	114	183	412	863	2041	5652

Conclusions

We illustrated a new method to solve the TDSE.
CP technique can be used

- in the spatial discretization of a time-dependent Schrödinger equation
- for efficient and accurate time stepping in the resulting ODE system