Available online at www.sciencedirect.com
SCIENCE DIRECT®
Computer Physics Communications 160 (2004) 129–139
Computer Physics Communications
www.elsevier.com/locate/cpc

The solution of stationary ODE problems in quantum mechanics by Magnus methods with stepsize control

J. Wensch [a,d,*], M. Däne [b,d], W. Hergert [b,d], A. Ernst [c]

[a] *Department of Mathematics and Informatics, Martin Luther University, Halle–Wittenberg, 06099 Halle, Germany*
[b] *Department of Physics, Martin Luther University, Halle–Wittenberg, 06099 Halle, Germany*
[c] *Max Planck Institute of Microstructure Physics, 06120 Halle, Germany*
[d] *Center of Computational NanoScience, Martin Luther University, Halle–Wittenberg, 06099 Halle, Germany*

Received 17 November 2003; accepted 4 March 2004

Abstract

In solid state physics the solution of the Dirac and Schrödinger equation by operator splitting methods leads to differential equations with oscillating solutions for the radial direction. For standard time integrators like Runge–Kutta or multistep methods the stepsize is restricted approximately by the length of the period. In contrast the recently developed Magnus methods allow stepsizes that are substantially larger than one period. They are based on a Lie group approach and incorporate exponential functions and matrix commutators. A stepsize control is implemented and tested. As numerical examples eigenvalue problems for the radial Schrödinger equation and the radial Dirac equation are solved. Further, phase shifts for scattering solutions for hydrogen atoms and copper are computed.

PACS: 02.70.-c; 71.15.-m

Keywords: Magnus methods; Computational techniques; Schrödinger and Dirac equation

1. Introduction

Large program packages devoted to problems in quantum chemistry or solid state theory contain as a core routines to solve the Schrödinger or Dirac equation. Starting from the very beginning of computational physics, a continuous interest in the development of new efficient techniques to solve those equations can be noticed, cf. [1–10]. There are special considerations for the calculation of bound states [1–3] or the scattering states [5,6]. Higher-order methods have been developed [4–7]. New numerical techniques like wavelets have been applied also to solve the Schrödinger equation [10].

The multi-particle problem for the electronic structure of solids is transformed in the framework of density functional theory [11] to an effective one-particle problem. The solution of this problem requires the solution of the Schrödinger respectively Dirac equation for one particle in a so-called effective potential. By an

* Corresponding author. FB Mathematik und Informatik, Martin Luther Universität Halle–Wittenberg, Postfach, 06099 Halle, Germany, Phone: +49 3455524754, Fax: +49 3455527033.
E-mail address: wensch@informatik.uni-halle.de (J. Wensch).

0010-4655/$ – see front matter
doi:10.1016/j.cpc.2004.03.004

ansatz with spherical harmonics the radial part is separated which leads to a system of linear ordinary differential equations with varying coefficients. We seek the eigenvalues of this system under boundary conditions with singularities.

In this work we present an algorithm to solve these eigenvalue problems. Eigenvalue problems for regular boundaries have been treated in [12] as well as singular boundary value problems. The treatment of singular eigenvalue problems constitutes a much more difficult task.

Nevertheless, the efficient treatment of the underlying direct problem (the initial value problem) is crucial for the solution of derived problems like eigenvalue problems. Among the well-known black box integrators for ordinary differential equations there are one-step methods like Runge–Kutta methods [13–16] and linear multistep methods like Adams [15] methods for nonstiff problems and BDF methods [16] for stiff problems. For second order problems Runge–Kutta–Nyström methods [17] constitute a very efficient choice, there are even special methods for oscillating problems [18].

We propose a method especially developed for linear differential equations with time dependent coefficients—the Magnus method. It is based on an expansion given by W. Magnus [19] for the solution of such equations. Magnus methods have been developed and investigated by several authors, see [20–26].

Our paper is organized as follows. In Section 2 we give an outline of the Magnus method. The complete algorithm to solve the eigenvalue problem is described in Section 3. The final section deals with numerical experiments for the Schrödinger and the Dirac equation, including scattering problems. The Magnus method with the stepsize selection algorithm of our choice is much superior to standard integration methods—whether explicit or implicit ones.

2. The Magnus method

2.1. Basics

For completeness we give a short description of the Magnus method and the underlying mathematics. For a more comprehensive overview see [26] or the more detailed papers [24,25].

We consider initial value problems for linear ordinary differential equations with varying coefficients

$$\frac{\mathrm{d}Y(t)}{\mathrm{d}t} = A(t)Y(t), \quad Y(t_0) = Y_0. \tag{1}$$

Assume for the moment that the solution $Y(t)$ is a matrix, i.e. we solve several systems simultaneously. The solution $Y(t)$ proceeds in the Lie group G whenever the coefficient matrix $A(t)$ belongs to the corresponding Lie algebra $\mathfrak{g}$ and the initial matrix Y_0 belongs to the Lie group G.

The Lie group is in general a nonlinear manifold. We parametrize it by a linear manifold—the Lie algebra—by means of the exponential map $\exp : \mathfrak{g} \mapsto G$

$$Y(t) = \exp\bigl(\sigma(t)\bigr) \cdot Y_0. \tag{2}$$

Instead of $Y(t) \in G$ we compute $\sigma(t) \in \mathfrak{g}$. In order to differentiate (2) we need the differential of the exponential map. It can be expressed in an elegant way by the function dexp

$$\mathrm{dexp}_B(C) := \left.\frac{\mathrm{d}}{\mathrm{d}t}\right|_{t=0} \exp(B + tC) \cdot \exp(-B), \tag{3}$$

where the linear function dexp_B can be given as a power series of the operator $\mathrm{ad}_B(\cdot) := [B, \cdot\,]$, that fixes the first argument in the matrix commutator $[A_1, A_2] := A_1A_2 - A_2A_1$, via

$$\mathrm{dexp}_B(C) = \sum_{k=0}^{\infty} \frac{1}{(k+1)!} \mathrm{ad}_B^k(C) =: \phi(\mathrm{ad}_B)(C). \tag{4}$$

The function ϕ in (4) maps the linear operator ad_B to the linear operator $\phi(\mathrm{ad}_B)$ that can be applied to the matrix C. This function ϕ is given by the analytic expression

$$\sum_{k=0}^{\infty} \frac{1}{(k+1)!} x^k = \frac{\mathrm{e}^x - 1}{\mathrm{x}} =: \phi(x). \tag{5}$$

From that we obtain a power expansion for the inverse function dexp^{-1} by the power series of $1/\phi(x)$, applied to the operator ad_B:

$$\begin{aligned}\mathrm{dexp}_B^{-1}(C) = \phi(\mathrm{ad}_B)^{-1}(C) &= \sum_{k=1}^{\infty} \frac{B_k}{k!} \mathrm{ad}_B^k(C) \\ &= C - \frac{1}{2}[B, C] \\ &\quad + \frac{1}{12}\bigl[B, [B, C]\bigr] + \cdots. \end{aligned} \tag{6}$$

Using the dexp^{-1}-map we differentiate (2) and insert (1) to obtain a differential equation for $\sigma(t)$

$$\begin{aligned}\sigma'(t) &= \operatorname{dexp}^{-1}_{\sigma(t)}\big(A(t)\big)\\ &= A(t) - \frac{1}{2}\big[\sigma(t), A(t)\big]\\ &\quad + \frac{1}{12}\big[\sigma(t), \big[\sigma(t), A(t)\big]\big] + \cdots. \end{aligned} \tag{7}$$

Note, that in the scalar case all commutators vanish and a simple integration remains. In the general case Picard iteration is applied to Eq. (7). This leads to the famous Magnus expansion—a series of iterated commutators and multidimensional integrals [19].

$$\begin{aligned}\sigma(t) &= + \int_0^t A(\tau_1)\,\mathrm{d}\tau_1\\ &\quad - \frac{1}{2}\int_0^t \left[A(\tau_1), \int_0^{\tau_1} A(\tau_2)\,\mathrm{d}\tau_2\right]\mathrm{d}\tau_1 + \cdots. \end{aligned} \tag{8}$$

Note, the series for $\operatorname{dexp}_B^{-1}$ converges whenever $\|\operatorname{ad}_B\| < 2\pi$. This is guaranteed for $\|B\| < \pi$ because $\|\operatorname{ad}_B(C)\| \leqslant 2\|B\|\|C\|$, see [23]. These conditions are rather restrictive, nevertheless, the Magnus method as described below will often work under less restrictive assumptions, see [23], too.

The discretization of the integrals in the Magnus expansion leads to what is called a Magnus method. A very elegant approach can be found in [21,22] where the series (8) for the interval $[t_n, t_n + h]$ is approximated by time-symmetric expressions. The matrix $A(t)$ is expanded in a power series at $t = t_n + h/2$

$$A(t) = \sum_{k=0} a_k \left(t - \left(t_n + \frac{h}{2}\right)\right)^k \tag{9}$$

which leads to an expansion for $\sigma(t_n + h)$ in odd powers of the stepsize h

$$\begin{aligned}\sigma(t_n + h) &= ha_0 + h^3\left(\frac{1}{12}a_2 + \frac{-1}{12}[a_0, a_1]\right)\\ &\quad + h^5\left(\frac{1}{80}a_4 + \frac{1}{80}[a_0, a_3] + \frac{1}{240}[a_1, a_2]\right.\\ &\quad + \frac{1}{360}[a_0, a_0, a_2] - \frac{1}{240}[a_1, a_0, a_1]\\ &\quad \left. + \frac{1}{720}[a_0, a_0, a_0, a_1]\right) + \mathcal{O}\big(h^7\big). \end{aligned} \tag{10}$$

The expression above is approximated by the time-symmetric integrals

$$B^{(i)} = \frac{1}{h^{i+1}} \int_{t_n}^{t_n+h} (t - t_n - h/2)^i A(t)\,\mathrm{d}t \tag{11}$$

with the desired accuracy. At this point numerical quadrature comes into play—ideally s Gauss points are used to obtain $\mathcal{O}(h^{2s})$-accuracy.

Casas et al. [21] produce a sequence of approximations $\sigma^{(2)} = \omega_1$, $\sigma^{(4)} = \omega_1 + \omega_3$, $\sigma^{(6)} = \omega_1 + \omega_3 + \omega_5$, where $\sigma^{(i)}$ has an error of order $\mathcal{O}(h^{i+1})$ for $i = 2, 4, 6$, by the formulas

$$\begin{aligned}\omega_1 &= hB^{(0)},\\ \omega_3 &= h^2\left[B^{(1)}, \frac{3}{2}B^{(0)} - 6B^{(2)}\right],\\ \omega_5 &= \left[\omega_1, \left[\omega_1, \frac{1}{2}hB^{(2)} - \frac{1}{60}\omega_3\right]\right] + \frac{3}{5}h\big[B^{(1)}, \omega_3\big]. \end{aligned} \tag{12}$$

2.2. Step size control with Magnus methods

An efficient implementation of a numerical method involves an adaptive stepsize selection algorithm. The choice of the stepsize is based on a uniformly distributed local error which requires an estimation for the local error. There are two concepts in error estimation for onestep methods—known as embedding and Richardson extrapolation. Here we follow the lines of embedding. Besides a method of higher order—say q—we use a second method of lower order p (the embedded method) for the purpose of error estimation.

The Magnus method offers a natural choice for the embedded method—to choose $\sigma = \sigma^{(4)} = \omega_1 + \omega_3$ to produce a embedded forth order solution $\widetilde{Y}_{n+1}$ and $\sigma = \sigma^{(6)} = \sigma^{(4)} + \omega_5$ to produce the sixth order solution Y_{n+1} (both via (2)), see [21,22].

The Lie group version of the local error is therefore given by

$$\begin{aligned}Y_{n+1}\widetilde{Y}_{n+1}^{-1} &= \exp\big(\sigma^{(6)}\big)\exp\big(-\sigma^{(4)}\big)\\ &= \exp\left(\sigma^{(6)} - \sigma^{(4)} + \frac{1}{2}\big[\sigma^{(6)}, \sigma^{(4)}\big]\right.\\ &\quad \left. + \mathcal{O}\big(\big\|\sigma^{(6)} - \sigma^{(4)}\big\|^2\big)\right),\\ \operatorname{err}_{\mathrm{est}} &= \left\|\sigma^{(6)} - \sigma^{(4)} + \frac{1}{2}\big[\sigma^{(6)}, \sigma^{(4)}\big]\right\| = \mathcal{O}\big(h^5\big). \end{aligned} \tag{13}$$

The drawback is that this error estimator works only in case of non-commutative matrices. In the convenient case when A commutes in $[t_0, t_E]$ then the Magnus series breaks down to pure quadrature, the error estimator vanishes. Further, the estimator neglects the quadrature error at all. To overcome this we propose (in contrast to [21,22]) an error estimator based on a lower order quadrature formula. We use a second method of fourth order, based on Gauss quadrature with the two nodes $c_{1/2} = (3 \pm \sqrt{3})/6$.

In general, there is an absolute tolerance *ATOL* and a relative tolerance *RTOL* prescribed. The code is forced to keep local error roughly below $ATOL + RTOL\|\sigma\|$. Whenever the estimated local error satisfies

$$\mathrm{err}_{\mathrm{est}} \leqslant TOL(\sigma) := ATOL + RTOL\|\sigma\| \tag{14}$$

the current step is accepted and a new stepsize h_{new} is computed via

$$h_{\mathrm{new}} = \alpha \max\bigl(r_{\min}, \min\bigl(r_{\max}, \bigl(\tfrac{TOL}{\mathrm{err}_{\mathrm{est}}}\bigr)^{1/(q+1)}\bigr)\bigr) h_{\mathrm{old}} \tag{15}$$

where q is the order of the estimator (the order of the lower order method). Suitable choices for the constants above are $\alpha \approx 0.9$, $r_{\max} = 5$, $r_{\min} = 0.2$. These constants serve to minimize the occurrence of rejected steps. A step is rejected if condition (14) is not satisfied. In that case the result is discarded and a new stepsize is computed from (15).

3. Numerical tests

The numerical solution of the Schrödinger and Dirac equation plays an important role in quantum mechanics and in solid states theory. There are two different types of problems. The first one is the calculation of bound states which is an eigenvalue problem and will be discussed in Section 3.2. The second kind of problems are scattering problems, where the solution is not normalizable. We will deal with this in Section 3.3. Both types of problems lead to oscillating solutions, so we will start the numerical comparison with an equation with oscillating solution in Section 3.1.

3.1. An oscillating example using the Bessel function

In our first example we want to show that the method is suitable for differential equations with strongly oscillating solutions.

$$y''(x) = -\left(100 + \frac{1}{4x^2}\right) y(x) \quad \text{with initial conditions}$$
$$y(1) = J_0(10), \quad y'(1) = \frac{1}{2} J_0(10) - 10 J_1(10), \tag{16}$$

where J_k denotes the Bessel function of first kind. The analytic solution of this differential equation is given by

$$y_{\mathrm{ex}}(x) = \sqrt{x}\, J_0(10x) \tag{17}$$

which is indeed a strongly oscillating function.

We compare the Magnus method (*MAGNUS6*) based on 3 Gauss points of order 6 with

GAUSS6 the classical Gauss formula itself (implicit, 6th order, [16]),

DOPRI5 a Runge–Kutta method (explicit, 5th order, [14]),

RKV4 the classical Runge–Kutta method (explicit, 4th order, [15]),

RKN86 a Runge–Kutta–Nyström method from Papakostas and Tsitouras (order 8, embedded solution of order 6, [17]),

RKN2 a Runge–Kutta–Nyström method from van der Houwen and Sommeijer constructed to solve oscillating problems. The general order is 2, but the method uses only one evaluation of the matrix A per step and has a reduced phase error (order 8), [18].

By that choice we cover a wide range of suitable methods. With the Gauss method we have included the implicit method that has the highest possible order for a prescribed number of stages. With DOPRI5 we have included one of the most efficient explicit Runge–Kutta formulas. For completeness we have added the widely used classical Runge–Kutta method. A very efficient class for second order differential equations are Runge–Kutta–Nyström methods. We use a high order method (RKN86) of Papakostas and Tsitouras and a low order method (RKN2) with improved phase order (order 8) of van der Houwen and Sommeijer.

The problem is solved on the interval [1, 100] by all 6 methods. In the first experiment we apply the methods with constant stepsize $h = 1.\mathrm{E}{-1}$ which results in

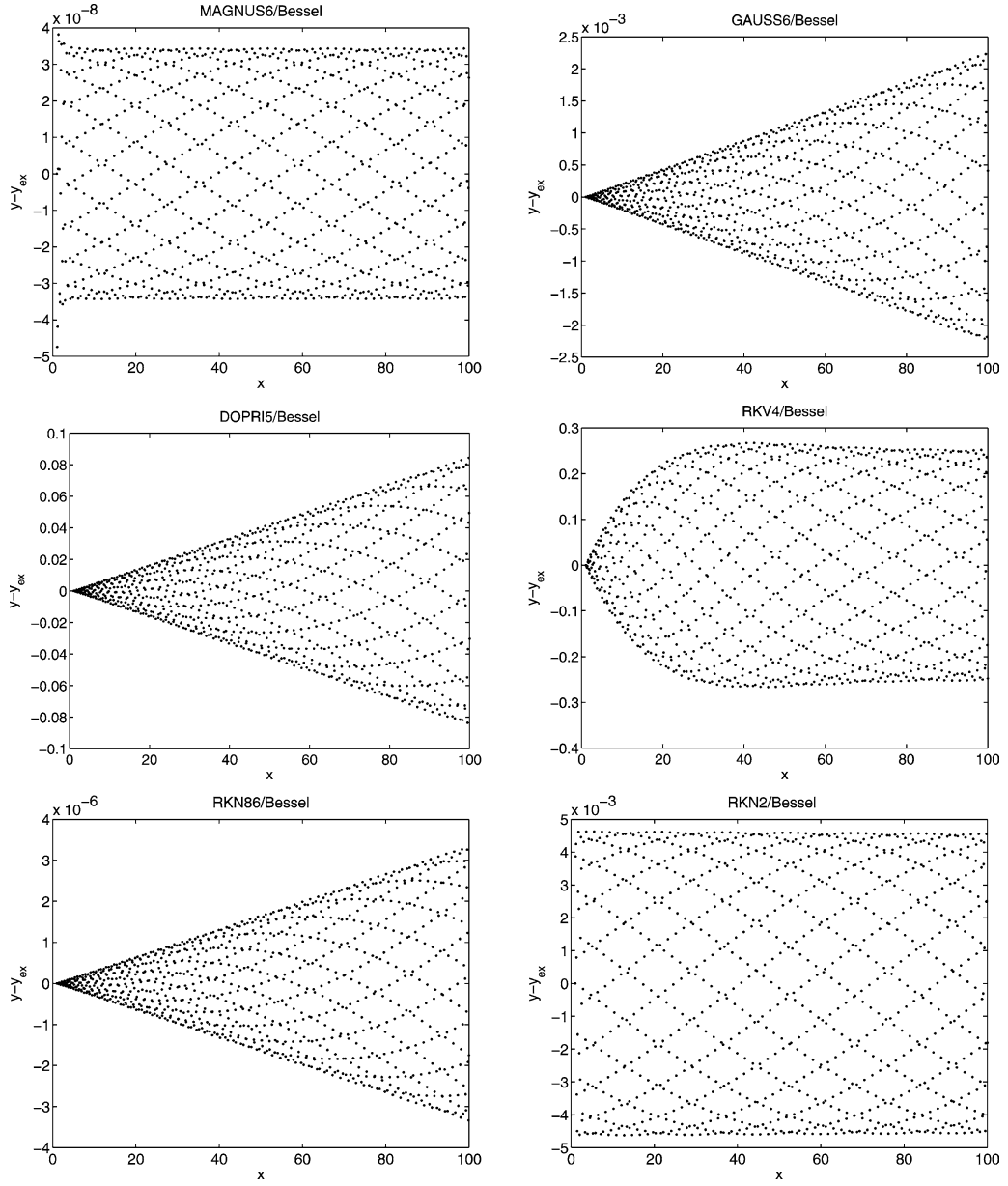

Fig. 1. Global error in the solution of Eq. (16) computed with constant stepsize $h = 1.\mathrm{E}{-1}$, $x_e = 100$, the oscillating example using the Bessel function.

990 steps for the complete interval. We compare the numerically computed values for y with the exact solution y_{ex} from (17). In Fig. 1 the difference at each intermediate point in the interval of integration is plotted by dots. The almost-periodic character of the solution causes the dots to form regular patterns.

The Magnus method keeps the global error below $4.\mathrm{E}{-8}$ which implies that for the Magnus method there is almost no phase shift in the numerical solution. The same is true for the method RKN2 of v.d. Houwen and Sommeijer which has order 8 in the phase space. For the other methods the error accumulates. For the

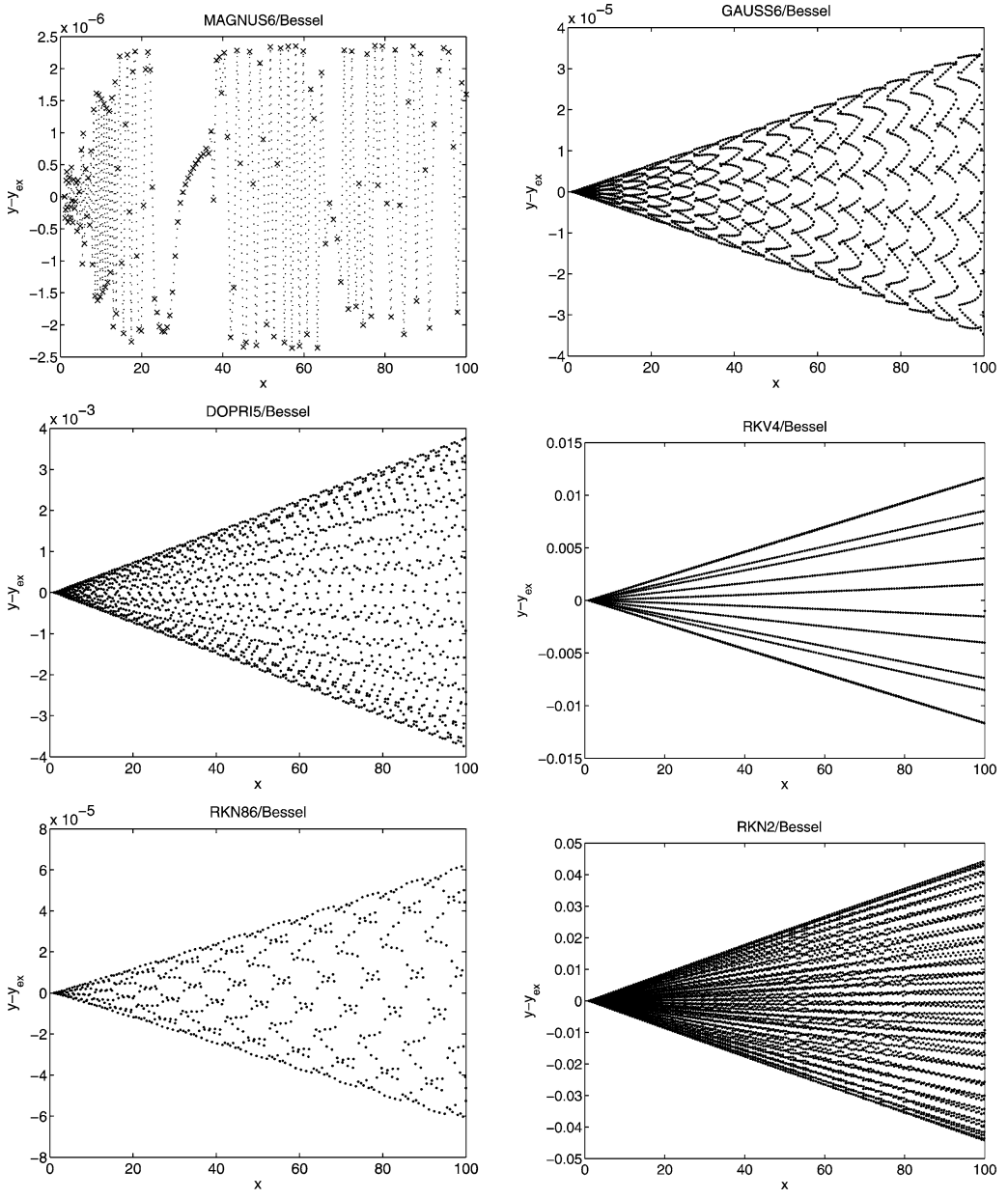

Fig. 2. Global error in the solution of Eq. (16) with stepsize control, $RTOL = 1.\mathrm{E}{-4}$, $x_e = 100$, the oscillating example using the Bessel function.

classical Runge–Kutta method RKV4 the solution in the endpoint is completely wrong, because this method generates a solution with decreasing amplitude.

In Fig. 2 the results with stepsize control for the 6 methods are given. We prescribed a relative tolerance of $RTOL = 1.\mathrm{E}{-4}$ and an absolute tolerance of $ATOL = 1.\mathrm{E}{-6}$. For the methods RKV4 and RKN2 we used Richardson extrapolation, whereas for the other 4 methods we used embedding. Note, that for the methods based on Gaussian quadrature of order 6 we have chosen the corresponding 4th order method based on two Gauss points as error estimator. The methods

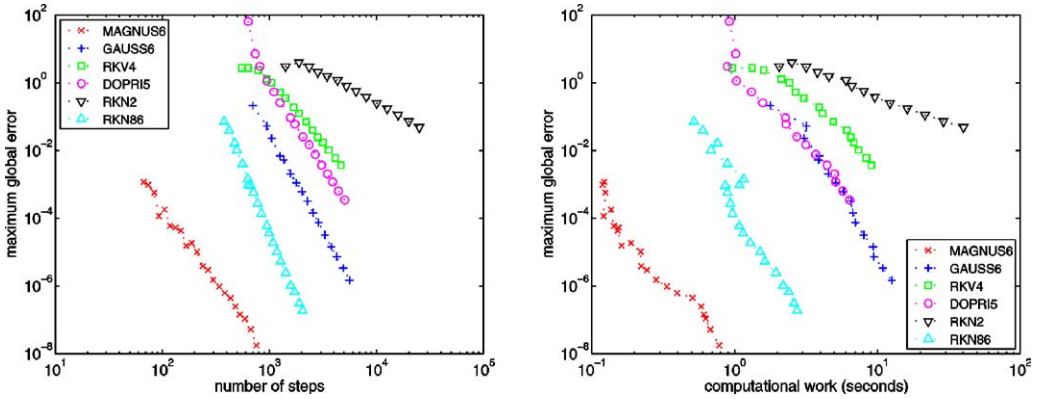

Fig. 3. Maximum global error versus number of steps and number of flops for all six methods for the oscillating example using the Bessel function.

DOPRI5 respectively RKN86 are equipped with 4th respectively 6th order error estimators.

The Magnus method managed the task with only 160 steps, second comes RKN86 with 800 steps. The other methods used approximately 2500 steps, except RKN2 which took 8000 steps.

The third experiment tests the efficiency of the step size control. The left picture in Fig. 3 displays the maximum global error versus the number of executed steps, discounting rejected steps. We remark that all step size selection algorithms worked quite satisfactory with less than 10 percent rejected steps. The performance of the methods is almost as expected. The Magnus method performs quite superior, whereas the other methods rank with respect to their order. RKN86 (order 8) is second, the Gauss method (order 6) is third, whereas DOPRI5 is fourth best.

For a realistic evaluation we have to take into account the computational effort. On the right picture in Fig. 3 the computing time is displayed. The Magnus method is again superior. One reason is that for $\mathbb{R}^{2\times 2}$ matrices there is an elegant way to compute the matrix exponential, see [26]. DOPRI5 performs now as good as the Gauss method because the Gauss method has to solve a linear system of dimension 6.

3.2. Generalized eigenvalue problem—H-Atom

3.2.1. The non-relativistic case—the Schrödinger equation

For the stationary one-particle Schrödinger equation we use a separation ansatz with radial and spherical components. For the spherical components we use the eigenfunctions of the spherical part of the Laplace operator (spherical harmonics). This leads to an eigenvalue problem for the radial component (E in Ryd, r in Bohr radii)

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + E - V(r)\right] R_l(r;E) = 0, \tag{18}$$

where the energy E is the eigenvalue of the eigenfunction $R_l(r;E)$. We consider here the case $l=0$, i.e. we solve for $R = R_0$. The potential V for the H-Atom is given by $V(r) = -2/r$. We end up with the eigenvalue problem

$$-R''(r) - \frac{2}{r}R(r) = ER(r), \quad R \in L_2\big([0,\infty)\big). \tag{19}$$

An asymptotic expansion of the solution near the boundaries gives boundary values at $r_{\min} \to 0$, $r_{\max} \to \infty$

$$R(r_{\min}) = r_{\min} - r_{\min}^2, \qquad R(r_{\max}) = 1, \tag{20}$$
$$R'(r_{\min}) = 1 - 2r_{\min},$$
$$R'(r_{\max}) = -\sqrt{-E} + \frac{1}{r_{\max}\sqrt{-E}}. \tag{21}$$

We integrate outwards from $r_{\min}$ up to r_{mid} and inwards from $r_{\max}$ up to r_{mid}. The resulting solutions and derivatives at r_{mid} are denoted by (y_l, y_l') for the outward integration respectively (y_r, y_r') for the inward integration. In order to have a continuously differentiable solution at r_{mid} the vectors (y_l, y_l') and (y_r, y_r') must be scalable such that they coincide, i.e. they must be linearly dependent. At a first glance

this seems to be equivalent to the fact that the angle between both vectors vanishes, but a more careful analysis reveals that the angle can be any multiple of π. By a restriction of the angle (say, to the interval $(-\pi/2, \pi/2]$) the resulting angle is not a continuous function of the values y_r, y_r', y_l, y_l'. To avoid these difficulties we compute at r_{mid} the sine of the angle ϕ, where ϕ is defined as the oriented angle between the vectors (y_r, y_r') and (y_l, y_l'). This is accomplished by the expression

$$\sin\phi = \frac{\Im z}{|z|} \quad \text{where}$$
$$z = (y_l + \mathrm{i}y_l')/(y_r + \mathrm{i}y_r'). \tag{22}$$

We use the Magnus method to solve Eq. (19) with a prescribed accuracy of $RTOL = 1.\mathrm{E}{-8}$, $ATOL = 1.\mathrm{E}{-10}$. We mention that the equation has to be transformed into a system of first order by introducing a new variable for the first derivative.

By that procedure we have computed the values given in Fig. 4 for $\sin\phi$ on a suitable E-grid. Based on that grid we start the method of secants to compute the zero of $\sin\phi$ in each interval where the sign changes. The iteration converges usually in four to six steps. The numerical values and the relative errors (compared with the known analytical solutions) are given in Table 1. Note, that the errors in the results are in the magnitude of the prescribed accuracy for the Magnus method.

Table 1
The values and relative errors for the 10 smallest energies of the hydrogen atom in the non-relativistic case (Schrödinger equation), computed as the zeros of Eq. (22)

No.	Energy (Ryd)	$-\log_{10}(\mathrm{err})$
1	−1.00000000	10.6
2	−0.24999982	6.2
3	−0.11111111	7.7
4	−0.06250000	8.8
5	−0.04000000	8.6
6	−0.02777778	8.4
7	−0.02040816	8.2
8	−0.01562500	7.4
9	−0.01234568	7.2
10	−0.00999999	7.1

3.2.2. *The relativistic case—the Dirac equation*

As a second example we consider the relativistic case and solve the analogous problem for the Dirac equation. The underlying physics is completely differ-

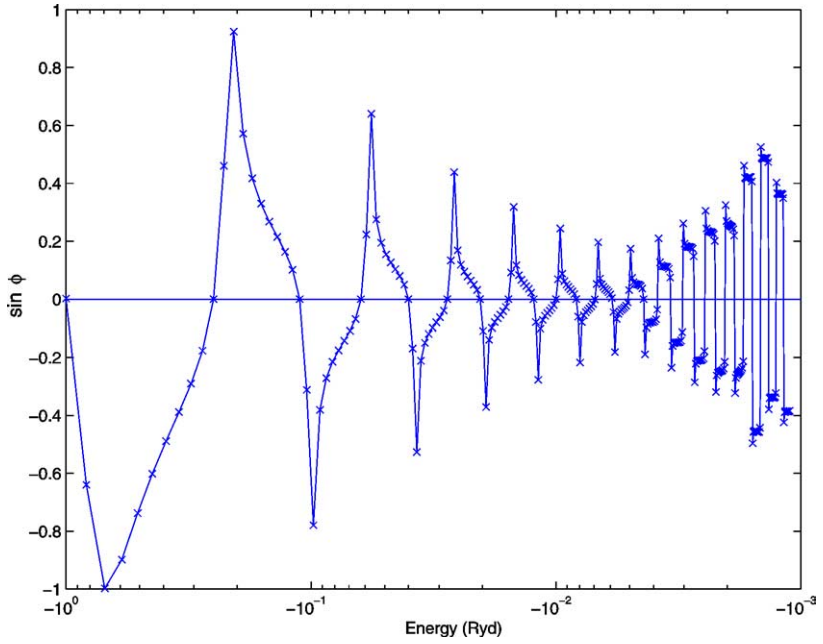

Fig. 4. The expression $\sin\phi(E)$ given by Eq. (22). The zeros of this function are the energy eigenvalues of the hydrogen atom.

ent but we end up with a linear system of first order, again.

The radial Dirac equations in atomic units is used: (E in Ryd, r in Bohr radii, fine structure constant $\alpha \approx 1/137$)

$$\frac{\partial u(r)}{\partial r} = -\frac{\kappa}{r}u(r) + \alpha\left(E + \frac{1}{r} + \frac{1}{\alpha^2}\right)v(r), \tag{23}$$

$$\frac{\partial v(r)}{\partial r} = \frac{\kappa}{r}v(r) - \alpha\left(E + \frac{1}{r} - \frac{1}{\alpha^2}\right)u(r). \tag{24}$$

In this example we calculate the bound state energies. The analytic solutions for the energies E (in Ryd) are given by

$$E = \frac{1}{\alpha^2}\left(1 + \frac{(\alpha)^2}{(n - |\kappa| + \sqrt{\kappa^2 - (\alpha)^2})^2}\right)^{-1/2} \tag{25}$$

where n and κ are quantum numbers.

The energies are found again by integrating the differential equation from $r_{\min} \to 0$ to r_{mid} and $r_{\max} \to \infty$ to r_{mid}. With the Magnus method of 4th order we found the lowest energies with more than 12 correct digits. The results are displayed in Table 2.

Table 2
The values and relative errors for the 16 smallest energies of the hydrogen atom in the relativistic case (Dirac equation, $\kappa = -1$)

No.	Energy (Ryd)	$-\log_{10}(\mathrm{err})$
1	18778.362409759477458237597 6024	16.4
2	18778.737414336827526994966 3197	14.0
3	18778.806860120926813806363 4978	15.5
4	18778.831166078056469359580 6602	15.9
5	18778.842416235024259663077 8280	16.0
6	18778.848527419329528242997 1848	16.5
7	18778.852212265134014046452 6484	16.5
8	18778.854603868948558442752 9829	17.0
9	18778.856243543089021841296 9261	16.9
10	18778.857416391446122361230 6639	16.7
11	18778.858284166030756523468 8809	16.3
12	18778.858944179406265106990 7587	16.5
13	18778.859457824774281675672 6824	16.4
14	18778.859865386483107840831 5079	16.7
15	18778.860194186359322543466 9875	16.6
16	18778.860463284880566448009 6311	16.8

3.3. Scattering problems

In the last two examples we consider scattering problems, where the solution is not normalizable and strongly oscillating. Here we use the Magnus method to calculate the values of physical interest—the phase shifts—where the ratio between the solution and the first derivative α_l at the endpoint r_M is relevant. The logarithmic derivative [27] is defined as

$$\alpha_l = \frac{\mathrm{d}}{\mathrm{d}r}\log R_l(r)|_{r=r_M} = \frac{R_l'(r_M)}{R_l(r_M)}. \tag{26}$$

First we solve the radial Schrödinger equation (18) for a radial potential well with the potential $V(r) = -V_0\,\Theta(a - r)$ for different energies and calculate the logarithmic derivative (26) (we choose $V_0 = (6.25)^2$Ryd and $a = 2$).

With the logarithmic derivative it is possible to calculate the phase shifts which are the shifts at the endpoint between solution with and without a scattering potential. In this example the phases shifts δ_l are given by

$$\cot\delta_l(E) = \left.\frac{\sqrt{E}n_l'(kr) - \alpha_l(E)n_l(kr)}{\sqrt{E}j_l'(kr) - \alpha_l(E)j_l(kr)}\right|_{r=r_M},$$
$$k = \sqrt{E}, \tag{27}$$

where j_l are spherical Bessel functions and n_l are spherical Neumann functions. The phase shifts are displayed in Fig. 5. A comparison shows good agreement between numerically computed values (symbols) and analytically calculated [28] phase shifts (solid lines).

The Korringa–Kohn–Rostoker (KKR) method is a multiple scattering approach to calculate the electronic structure of solids in the framework of density functional theory. Using a KKR code, described in [29], the spherically symmetric potential of Cu is numerically calculated in the atomic sphere approximation. In Fig. 6 the potential (left) and the resulting phase shifts are given. The Magnus method works efficiently and reliably in this example. The resonance at approximately 0.45 Ryd for channel $l = 2$ is computed with satisfying accuracy.

4. Conclusion

Various problems from solid state physics lead to differential equations with oscillating solutions. We

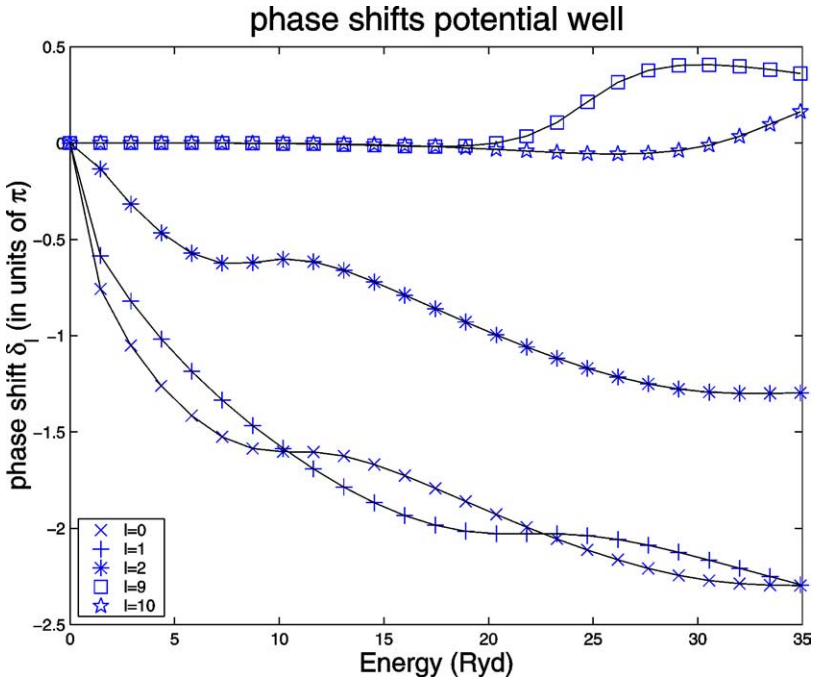

Fig. 5. Phase shifts δ_l for scattering on a radial potential well ($V_0 = -(6.25)^2$Ryd, radius 2 a.u.). Analytical values are given by solid lines, numerically computed are given by symbols, see legend.

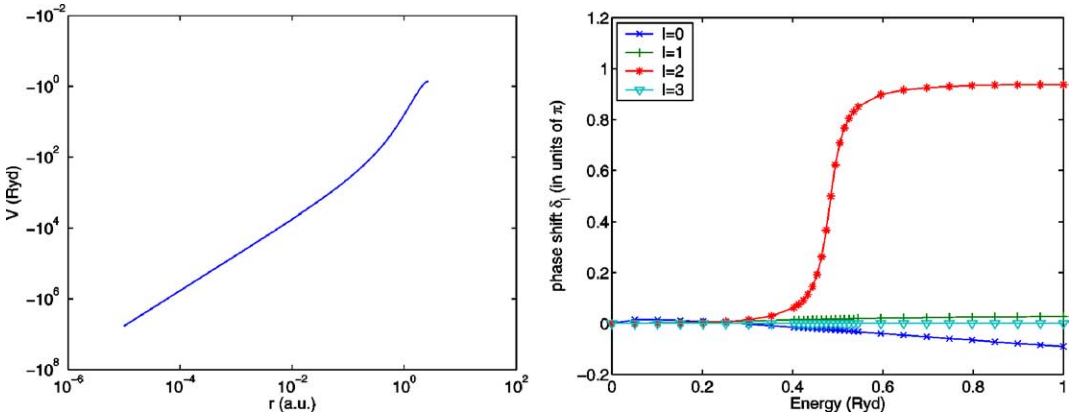

Fig. 6. Numerically computed potential for copper ($1.\mathrm{E}{-5} \leqslant r \leqslant r_M = 2.66$) and the resulting phase shifts for angular momentum $l = 0, 1, 2, 3$.

have considered here the radial Schrödinger and Dirac equation for bounded states as well as for scattering solutions. As the method of choice for these problems we propose the Magnus method. This method is especially adapted to first order linear equations with varying coefficients. By use of standard transformations it can be applied to systems of higher order, like the Schrödinger equation, too. The numerical experiments illustrate the superior performance of the method compared with classical numerical onestep methods. The proposed stepsize selection algorithm works efficiently and reliably.

An advantage is that the method is very easy to implement. Further, the method solves the variational equations per se and is therefore well suited for the solution of boundary value and eigenvalue problems.

One drawback is that the evaluation of the matrix exponential function is needed. This may lead to additional cost for higher order systems. The incorporation of Magnus methods for problems of higher dimension is subject of ongoing research.

References

[1] R.G. Gordon, New method for constructing wavefunctions for bound states and scattering, J. Chem. Phys. 51 (1969) 14–25.

[2] A.C. Allison, The numerical solution of coupled differential equations arising from the Schrödinger equation, J. Comput. Phys. 6 (1970) 378–391.

[3] B.R. Johnson, The renormalized Numerov method applied to calculating bound states of the coupled-channel Schrödinger equation, J. Chem. Phys. 69 (1978) 4678–4688.

[4] A.G. Abrashkevich, D.G. Abrashkevich, M.S. Kaschiev, I.V. Puzynin, Finite-element solution of the coupled-channel Schrödinger equation using high-order accuracy approximations, Comput. Phys. Commun. 85 (1995) 40–64.

[5] T.E. Simos, Eighth order methods for accurate computations for the Schrödinger equation, Comput. Phys. Commun. 105 (1997) 127–138.

[6] T.E. Simos, Eighth order method for accurate computations for the elastic scattering phase-shift problem, Internat. J. Quant. Chem. 68 (1998) 191–200.

[7] T.E. Simos, An accurate eighth order exponentially-fitted method for the efficient solution of the Schrödinger equation, Comput. Phys. Commun. 125 (2000) 21–59.

[8] G. Papageorgiou, Ch. Tsitouras, I.Th. Famelis, Explicit Numerov type methods for second order IVPs with oscillating solutions, Internat. J. Modern Phys. C 12 (5) (2001) 657–666.

[9] J.D. Praeger, Relaxational approach to solving the Schrödinger equation, Phys. Rev. A 63 (2001) 022115, 10 pages.

[10] P. Fischer, M. Defranceschi, Numerical solution of Schrödinger equation in a wavelet basis for hydrogen-like atoms, SIAM J. Numer. Anal. 35 (2001) 1–12.

[11] I. Turek, V. Drchal, J. Kudrowský, M. Šob, Electronic Structure of Disordered Alloys, Surfaces and Interfaces, Kluwer, Boston, 1997.

[12] H.B. Keller, Numerical Solution of Two Point Boundary Value Problems, SIAM, Philadelphia, 1990.

[13] J. Butcher, The Numerical Analysis of Ordinary Differential Equations: Runge–Kutta and General Linear Methods, Wiley, New York, 1987.

[14] J.R. Dormand, P.J. Prince, New Runge–Kutta algorithms for numerical simulation in astronomy, Celestial Mechanics 18 (1878) 223–232.

[15] E. Hairer, S.P. Nørsett, G. Wanner, Solving Ordinary Differential Equations I. Nonstiff Problems, Springer-Verlag, Berlin, 1993.

[16] E. Hairer, G. Wanner, Solving Ordinary Differential Equations II. Stiff and Differential–Algebraic Problems, Springer-Verlag, Berlin, 1996.

[17] S.N. Papakostas, Ch. Tsitouras, High phase-lag order Runge–Kutta and Nystrom pairs, SIAM J. Sci. Comput. 21 (1999) 747–763.

[18] P.J. van der Houwen, B.P. Sommeijer, Explicit Runge–Kutta–Nyström methods with reduced phase errors for computing oscillating solutions, SIAM J. Numer. Anal. 24 (3) (1987) 595–617.

[19] W. Magnus, On the exponential solution of differential equations for a linear operator, Comm. Pure Appl. Math. 7 (1954) 649–673.

[20] S. Klarsfeld, J.A. Oteo, Recursive generation of high-order terms in the Magnus expansion, Phys. Rev. A 39 (1989) 3270–3273.

[21] S. Blanes, F. Casas, J. Ros, Improved high order integrators based on the Magnus expansion, BIT 40 (2002) 434–450.

[22] S. Blanes, F. Casas, J. Ros, High order optimized geometric integrators for linear differential equations, BIT 42 (2002) 262–284.

[23] M. Hochbruck, C. Lubich, On Magnus integrators for time-dependent Schrödinger equations, SIAM J. Numer. Anal. 41 (3) (2003) 945–963.

[24] A. Iserles, S.P. Nørsett, On the solution of linear differential equations in Lie groups, Phil. Trans. Royal Soc. A 357 (1999) 983.

[25] A. Iserles, A. Marthinsen, S.P. Nørsett, On the implementation of the method of Magnus series for linear differential equations, BIT 39 (1999) 281–304.

[26] A. Iserles, H.Z. Munthe-Kaas, S.P. Nørsett, A. Zanna, Lie-group methods, Acta Numer. 9 (2000) 215–365.

[27] A. Gonis, Green Functions for Ordered and Disordered Systems, North-Holland, Amsterdam, 1992.

[28] A. Messiah, Quantum Mechanics, North-Holland, Amsterdam, 1961.

[29] A. Ernst, M. Lüders, W.M. Temmerman, Z. Szotek, G.A. van der Laan, Theoretical study of magnetic layers of nickel on copper; dead or alive?, J. Phys. Condens. Matter 12 (2000) 5599–5606.