# An exact analysis of the optical Kerr effect for an arbitrary field strength including nonlinear effects

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An optical Kerr effect, which is the transient electric birefringence of isotropic molecular fluids when the molecules align themselves with external field, is investigated. Calculations have been carried out on the rotational diffusion of rod-like molecules in the presence of an arbitrary field strength. We will provide an exact recurrence relation with nonlinear effects and this recurrence relation is solved numerically to see how the nonlinearity affects the answer for various field strengths.

## I. INTRODUCTION

Molecular dynamic properties have been studied by applying an external field to initially isotropic liquids. When an external field is applied to initially isotropic molecular liquids there is molecular reorientation, i.e., birefringence or induced anisotropy in the system. As a result the refractive index is changed. This phenomenon is called the Kerr effect or optical Kerr effect when the field is optical. Soileau et al.,[1] described a technique by which self-focusing and laser-induced breakdown were used to make an optical power limiter having a picosecond respond time. When an intense laser beam was applied to isotropic molecular liquids such as carbon disulphide or nitrobenzene, the self-focusing (intensity dependent refraction) to the incident laser beam was observed in a picosecond time scale. The nonlinear effect was also included in this experiment. Commerical nematic and twisted-nematic liquid crystal displays are also made using the Kerr effect. Computer simulation on simple liquids provides useful information on molecular dynamic properties.[2] However, complex molecules hinders this kind of approach due to the expensive computing time.

In order to interpret such experimental results it is necessary to describe the orientational motion of a molecule of liquids. In a dense fluid a molecule will experience many collisions as it rotates from position to position. This view of the dynamics of molecular liquids suggests that the process is diffusion-like in nature. Although a molecule in a fluid rotates along a deterministic trajectory according to Euler's equations of motion, this motion is sufficiently complex so that it may be viewed as proceeding through a rather randomly chosen path. Since the orientational motion of a molecular liquid is affected by collisions and a similarly complex trajectory, it is possible to develop a diffusion model for orientational dynamics. The static and dynamic properties of the optical Kerr effect are the primary interest in this study.

## II. THEORY

If the molecule has cylindrical symmetry, then the angular distribution function satisfies the Smoluchowski equation,[3] which can be easily derived from the diffusion model

$$\frac{\partial \rho(\theta,t)}{\partial t} = \frac{D}{\sin \theta} \frac{\partial}{\partial \theta}$$
$$\times \left\{ \sin \theta \left[ \frac{\partial \rho(\theta,t)}{\partial \theta} + \frac{1}{k_B T} \frac{\partial V}{\partial \theta} \rho(\theta,t) \right] \right\}, \quad (1)$$

where $D$ is the rotational diffusion coefficient, $k_B$ the Boltzmann constant, $T$ the temperature of the system, and $\theta$ the angle between the molecular axis and the direction of the applied field. $V(\theta,t)$ is the potential energy due to time-varying external field.

In this study we will derive the simple form of recurrence relation having nonlinear terms from this equation and give the exact numerical solution with nonlinear terms for various field strengths to show how the nonlinearity affects the answer. Furthermore, this exact numerical solution may be used to compare with the approximate solutions by other methods.

For a rod-like molecule which has cylindrical symmetry, the potential energy due to the applied field may be given as follows.

$$V(\theta,t) = -\mu E(t) \cos \theta - \tfrac{1}{2}\Delta\alpha E^2(t)\cos^2 \theta$$
$$- \tfrac{1}{6} \Delta\beta E^3(t)\cos^3(\theta) - \tfrac{1}{24}\Delta\gamma E^4(t)$$
$$\times \cos^4 \theta + \cdots, \quad (2)$$

where $\mu$ is the permanent dipole moment along the axis of the molecule, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, the difference of the molecular polarizability between parallel and perpendicular components to the molecular axis. Similarly, $\Delta\beta$ and $\Delta\gamma$ are the differences of its hyperpolarizability, respectively. The third and fourth terms represent nonlinear effects.

One may formally solve Eq. (1) by expanding the distribution function $\rho(\theta,t)$ in Legendre polynomials,

$$\rho(\theta,t) = \sum_{n=0}^{\infty} a_n(t)P_n(\cos \theta), \quad (3)$$

where

$$a_n(t) = \frac{2n+1}{2} \int_{-1}^{1} \rho(\theta,t)P_n(\cos \theta)d(\cos \theta). \quad (4)$$

Substituting $\rho(\theta,t)$ into Eq. (1) and multiplying $P_m(\theta)$ on both sides of Eq. (1) and integration over the angle $\theta$, one

can simply obtain the recurrence relation as follows:

$$\frac{da_0}{d\tau} = 0, \quad \tau = Dt,$$

$$\frac{da_n(\tau)}{d\tau} = cm_4 a_{n-4}(\tau) + cm_3 a_{n-3}(\tau) + cm_2 a_{n-2}(\tau)$$

$$+ cm_1 a_{n-1}(\tau) + c_0 a_n(\tau) + cp_1 a_{n+1}(\tau)$$

$$+ cp_2 a_{n+2}(\tau) + cp_3 a_{n+3}(\tau) + cp_4 a_{n+4}(\tau),$$
(5)

where these coefficients are

$$cm_4(\tau) = 4h(\tau)(n+1)n(n-1)(n-2)(n-3)/(2n-7)(2n-5)(2n-3)(2n-1),$$

$$cm_3(\tau) = 3g(\tau)(n+1)n(n-1)(n-2)/(2n-5)(2n-3)(2n-1),$$

$$cm_2(t) = 2f(\tau)(n+1)n(n-1)/(2n-3)(2n-1)$$

$$+ 4h(\tau)(n+1)n(n-1)(2n^2-n-9)/(2n-5)(2n-3)(2n-1)(2n+3),$$

$$cm_1(\tau) = e(\tau)n(n+1)/(2n-1) + 3g(\tau)n(n+1)(n^2+n-3)/(2n-3)(2n-1)(2n+3),$$

$$c_0(\tau) = -n(n+1) + 2f(\tau)n(n+1)/(2n-1)(2n+3)$$

$$+ 12h(\tau)n(n+1)(n^2+n-3)/(2n-3)(2n-1)(2n+3)(2n+5),$$

$$cp_1(\tau) = -e(\tau)n(n+1)/(2n+3) - 3g(\tau)n(n+1)(n^2+n-3)/(2n-1)(2n+3)(2n+5),$$

$$cp_2(\tau) = -2f(\tau)n(n+1)(n+2)/(2n+3)(2n+5)$$

$$- 4h(\tau)n(n+1)(n+2)(2n^2+5n-6)/(2n-1)(2n+3)(2n+5)(2n+7),$$

$$cp_3(\tau) = -3g(\tau)n(n+1)(n+2)(n+3)/(2n+3)(2n+5)(2n+7),$$

$$cp_4 = -4h(\tau)n(n+1)(n+2)(n+3)(n+4)/(2n+3)(2n+5)(2n+7)(2n+9),$$

and the field strengths in these coefficients are

$$e(t) = \mu E(t)/kT, \quad f(t) = \Delta\alpha E^2(t)/2kT,$$

$$g(t) = \Delta\beta E^3(t)/6kT, \quad h(t) = \Delta\gamma E^4(t)/24kT.$$

Equation (5) is an infinite set of coupled first-order differential equations. Note that for the special case, $e(t) = f(t) = g(t) = h(t) = 0$, i.e., no external field is applied, then this equation gives the solution of simple Debye diffusion theory.

Various authors have used an approximate method to solve Eq. (5). Benoit[4] tried to get $a_2$ only for limiting low fields. Schwarz[5] calculated the distribution function and $a_2$ at infinitely high field strength with pure induced dipole term only. O'Konski *et al.*[6] also did similar calculations but with permanent dipole terms only. Nishinari and Yoshioka[7] began with operator methods but obtained similar results. Morita and Watanabe[8] obtained $a_2$ in a form of Laplace transform for an arbitrary field strength. However, nonlinear effects were not considered by any of these works.

We will introduce the Runge–Kutta method to solve this equation numerically, which will be explained in the Appendix. We have assumed the potential energy to be time independent, i.e., at $t = 0$ a constant external field is applied although optical fields are usually used in the real experiment.[1,9] This assumption can be argued as follows. Because the frequency of optical fields in experiment is high, $10^{15}$–$10^{17}$ Hz, the torque on a molecule varies with a period of about $10^{-15}$–$10^{-17}$ s. This is much faster than any of the molecular processes in the liquid. Hence only the average torque due to the external field needs to be considered. In other words, the time varying external field can be treated as the static constant field.

Since the system is initially isotropic, $a_0$ is time independent and is chosen to be one, and $a_n|_{n\neq 0} = 0$ at $t = 0$. With these boundary conditions, $a_n(t)$ for $t > 0$ is obtained numerically. Because the order of $a_n(t)$ is infinite, some truncation procedures must be adapted to solve this set of equations numerically. On physical grounds, one expects that the dominant $a_n$'s will be those with small $n$. For large $n$, $a_n(t)$ must go to zero if the expansion Eq. (5) is to be convergent. Thus numerically the truncation is implemented by keeping only a finite number of $a_n(t)$ and assuming that the rest are negligible. The number of terms in the expansion which must be kept is determined empirically. For large fields, more $a_n$ needs to be kept. This is tested by simply solving the equation twice, once with a very large number of $a_n$ to see if the solution changes appreciably as more $a_n$ are retained. Generally speaking, $a_n$ for $n < 50$ was sufficient for all cases in this work.

The equilibrium, time-independent solution may be obtained from Eq. (5) as the time goes to infinity, or by solving Eq. (1) when the left-hand side of the equation is equal to zero. The latter solution can be simply obtained from physical intuitions as follows. When the system is in equilibrium in the presence of the external field, the density which expresses the angular distribution must be given by the Boltzmann distribution, i.e.,

$$\rho(\theta) = \frac{\exp(-V(\theta)/kT)}{\int \exp(-V(\theta)/kT)d\cos\theta}.$$
(6)

The equilibrium values of $a_n$ are obtained from this density, by taking its thermal average and also noting from Eqs. (3) and (4) that $a_n$ is closely related to the Legendre polynomials,

$$\frac{1}{2n+1}\langle a_n\rangle = \langle p_n\rangle = \frac{\int P_n(x)\exp[-V(x)/kT]dx}{\int \exp(-V/kT)dx},$$

(7)

where $1/2n + 1$ is the normalizing factor of $\langle P_n\rangle$. Thus the solution of Eq. (5) can be monitored by the results of Eq. (7).

## III. RESULTS AND DISCUSSIONS

We will solve numerically the infinitely coupled first-order differential Eq. (5) by the Runge–Kutta method. The optical Kerr effect is represented by $\langle P_2[\cos(\theta)]\rangle$ where the bracket indicates the thermal averages. This quantity is important since it is related to the dielectric dispersion and the refractive index directly.[7]

When the linearly polarized field is applied, this value is zero initially and becomes one for a perfectly ordered state. The situation is however, somewhat different for a circularly polarized field. For a circularly polarized field, this value is zero initially and becomes $-0.5$ for perfectly ordered state. Since the general procedure in the calculation of $\langle P_2\rangle$ is exactly the same for both fields, we will consider only the case of linearly polarized fields.

### A. Polar molecular system

For the polar molecular system all the even terms in the potential energy must be zero from the antisymmetry of the molecule, i.e., $V(-x) = -V(x)$. The system is initially isotropic and the external field is suddenly applied at $t = 0$, i.e., $a_0 = 1$, $a_n|_{n\neq 0} = 0$ at $t = 0$. As mentioned in the previous section, this field can be treated as a time-independent field even though it is an optical field. Thus the potential energy due to the external field is represented as follows.

$$\frac{V(\theta)}{kT} = -e_0\cos\theta - g_0\cos^3\theta.$$

(8)

The molecules will be redistributed by this external field and thus $a_n$ is not equal to zero any longer for $t > 0$.

Shown in Fig. 1 is the dynamic response of the order parameter $\langle P_2\rangle$ in terms of the dimensionless time $(Dt)$ for various nonlinear field strengths. We chose relatively low field strength, $e_0$ ( $= \mu E/kT$) $= 0.4$. The bottom solid line does not include a nonlinear term. The relative nonlinear field strength ( $g_0/e_0 = \Delta\beta E^2/6\mu$) is chosen to be 0.8, 0.6, 0.4, 0.2 from the top to the bottom line, respectively. The molecules will be redistributed and the instaneous birefringence will be established as the time goes and the molecule reaches a new equilibrium state as the time goes to the infinity. Since relatively low field strength is used, the absolute difference of the order parameter between each line of the nonlinear terms is negligible although the relative difference between them is significant (note that the maximum scale of the order parameter is 0.05).

Figure 2 is similar to Fig. 1, but is in terms of a relatively high field strength ($e_0 = 5$). The general shape is very much the same as Fig. 1, but the order parameter reaches an equilibrium state faster than that of Fig. 1, and the new equilibrium values of the order parameter is much larger than those of Fig. 1. The nonlinear effect is very significant and cannot be negligible at this time for both relative and absolute magnitudes. One important thing to notice is that the slope, i.e., $d\langle P_2(x)\rangle/dt$ is zero at $t = 0$, which agrees with O'Konski's prediction in his experiment.[10]

Figure 3 shows equilibrium values of the order parameter in terms of the field strength $e_0$. The bottom solid line in the figure is the one without a nonlinear term and the lines from top to bottom show the nonlinear effects with relative nonlinear field strength, $g_0/e_0 = 0.8, 0.6, 0.4, 0.2$, respectively. This figure clearly shows how serious the nonlinear effects are. As the field gets larger, the nonlinear effects are more serious. Even for relatively small nonlinear field strength, $g_0/e_0 = 0.2$ (the second solid line from the bottom), the difference cannot be negligible. It is also noted that the slope, $d\langle P_2(x)\rangle/de_0$ at $e_0 = 0$ is zero which may not be calculable from the other theory.
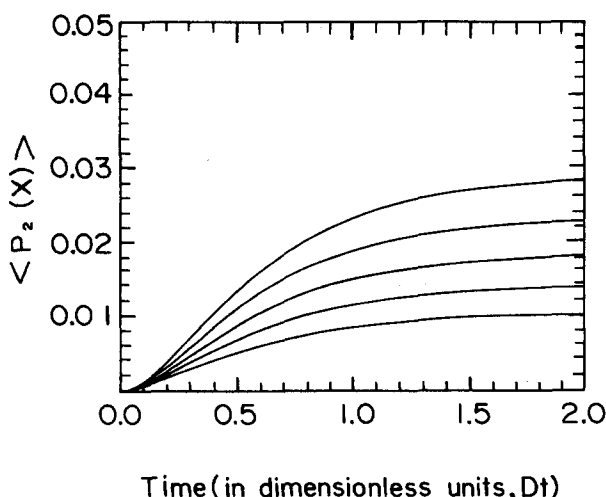


FIG. 1. Dynamic response of the order parameter $\langle P_2(x)\rangle$ in terms of dimensionless time $Dt$ of the polar system for various nonlinear field strength $g_0/e_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectively, where $e_0$ is 0.4, relatively low field strength.
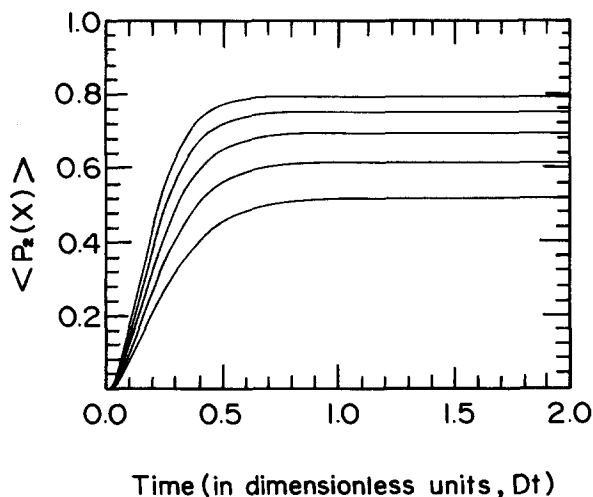


FIG. 2. Dynamic response of the order parameter $\langle P_2(x)\rangle$ in terms of dimensionless time $Dt$ of the polar system for various nonlinear field strength $g_0/e_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectivley, where $e_0$ is 5.0, relatively high field strength.
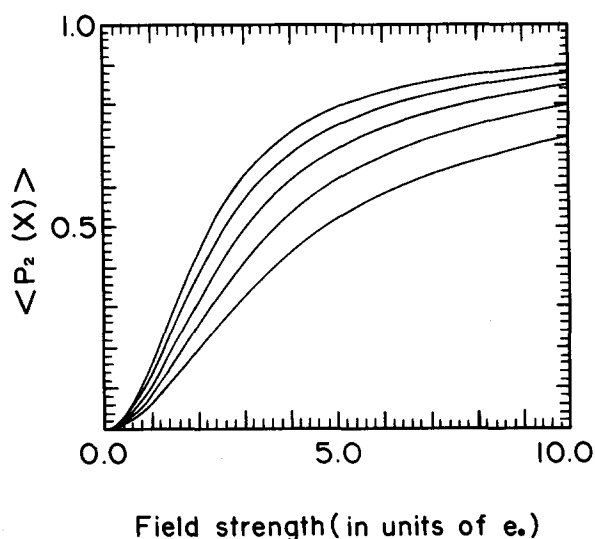
FIG. 3. Equilibrium values of the order parameter in terms of field strength $e_0$ of the polar system for relative nonlinear field strength $g_0/e_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectively.



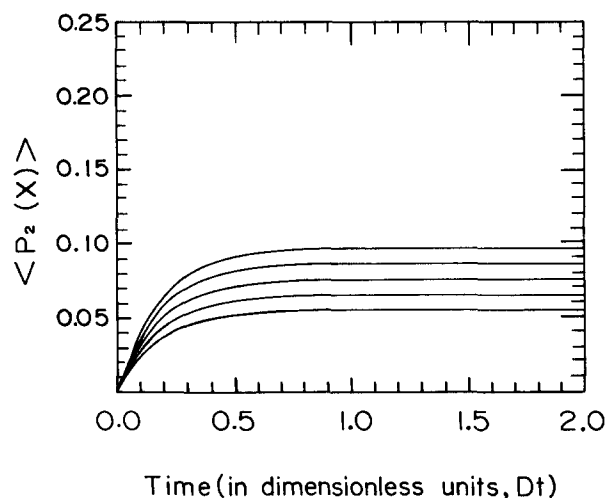Time (in dimensionless units, Dt)

FIG. 5. Dynamic response of the order parameter $\langle P_2(x) \rangle$ in terms of dimensionless time $Dt$ of the nonpolar system for various nonlinear field strength $h_0/f_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectively, where $f_0$ is 5.0, relatively high field strength.

## B. Nonpolar molecular system

The nonpolar molecular system does not have a permanent dipole moment but has an induced dipole moment. Because of the symmetry of the molecule the potential energy due to the external field satisfies the condition $V(-x) = V(x)$ and therefore, all the odd terms of $a_n(t)$ must be equal to zero. The same initial condition as before may be given in this system, i.e., $a_0 = 1$, $a_n|_{n \neq 0} = 0$ at $t = 0$ and the constant field is suddenly applied at time $t = 0$. Then the potential energy due to the field is expressed,

$$\frac{V(\theta)}{kT} = -f_0 \cos^2 \theta - h_0 \cos^4 \theta. \tag{9}$$

Shown in Fig. 4 is the dynamic response of the order parameter as a function of the dimensionless time ($Dt$) for various nonlinear field strengths, $h_0/f_0 ( = \Delta \gamma E^2/ 12 \Delta \alpha) = 0.8, 0.6, 0.4, 0.2, 0$, from the bottom to the top line, respectively (zero means that it does not include the nonlinear term). Relatively low field strength is chosen, i.e., $f_0 = 0.4$. The similar behaviors to Fig. 1 are shown here. However, there are several differences between them. The slope $d \langle P_2 \rangle/dt$ at $t = 0$ is not zero but constant for the nonpolar system. This proves that O'Konski's prediction[10] in his paper was correct.

The order parameter reaches an equilibrium state much faster by a factor of 3 than that of the polar molecular system
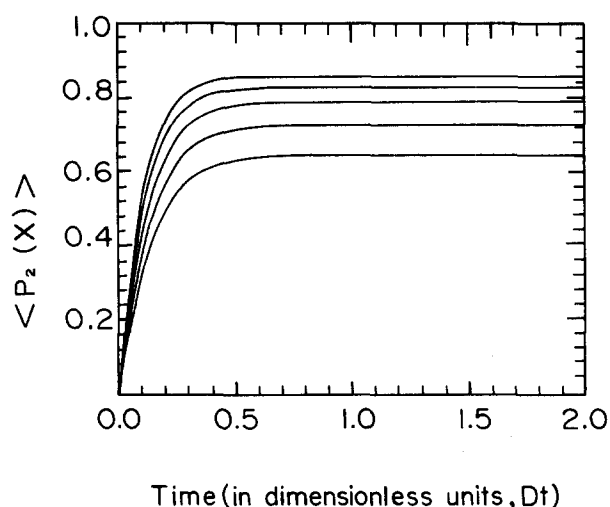


Time (in dimensionless units, Dt)

FIG. 4. Dynamic response of the order parameter $\langle P_2(x) \rangle$ in terms of dimensionless time $Dt$ of the nonpolar system for various nonlinear field strength $h_0/f_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectively, where $f_0$ is 0.4, relatively low field strength.



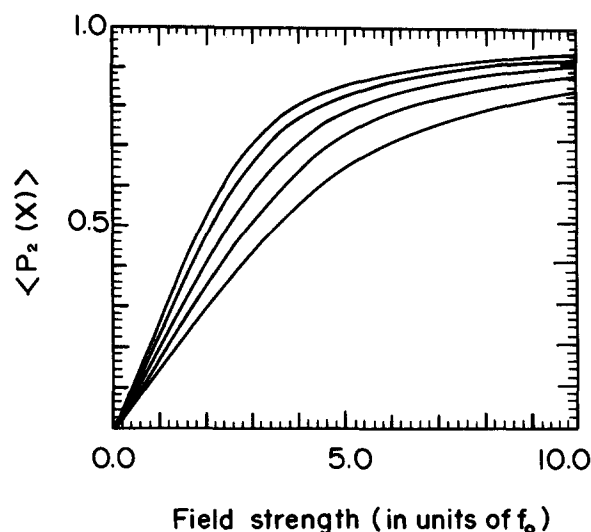Field strength (in units of $f_0$)

FIG. 6. Equilibrium values of the order parameter in terms of field strength $f_0$ of the nonpolar system for relative nonlinear field strength $h_0/f_0 = 0.8, 0.6, 0.4, 0.2, 0$, from the top to the bottom line, respectively.

and its equilibrium values are much larger by a factor of 3 (note that the scales are different in Fig. 1 and Fig. 4). These differences will be smaller as the field strength becomes larger. Figure 5 shows this. Now the differences are greatly reduced compared to Fig. 2 but their differences in equilibrium state still exist and the nonpolar system responds still faster. Shown in Fig. 6 is the equilibrium values of $\langle P_2 \rangle$ in terms of the field strength ($f_0 = \Delta \alpha E^2 / 2kT$). The curves from the top to the bottom indicate $\langle P_2(x) \rangle$ for relative nonlinear field strength, $h_0/f_0 = 0.8, 0.6, 0.4, 0.2, 0$, respectively. The initial slope, $d \langle P_2 \rangle / df_0$ is not zero but constant for the nonpolar system. Furthermore, the order parameters in Fig. 6 are larger than those in Fig. 3. What it means is that if one wants to make an optical power limiter or optical switches it is better to choose the nonpolar molecular system than the polar system since the former is faster and more effective (larger equilibrium values).

## IV. CONCLUSIONS

We have solved the Smoluchowski equation and obtained the recurrence relation including nonlinear effects. This recurrence relation is solved numerically and applied to the polar and nonpolar molecular systems. It is shown that the nonlinear effects cannot be negligible even for relatively low field strength. It is also observed that the nonpolar system responds faster than the polar system and the Kerr effect is larger than that of the polar system.

## APPENDIX

We will illustrate how the infinitely coupled first-order differential equation can be solved numerically.

Let the first derivative of function $a_n$ be

$$\dot{a}_n(t) = f(a_n, a_i, t), \qquad (A1)$$

where the dot indicates the derivative of $a_n$ with respect to $t$ and $i \neq n$. For the given initial condition at time $t$ [for example, $a_0(0) = 1$, $a_n |_{n \neq 0} = 0$], the value at $t + h$, $a_n(t + h)$ where $h$ is the small time interval, may be obtained from the information of the initial condition at $t$. The best guess is to expand $a_n(t + h)$ in a Taylor series for small $h$,

$$a_n(t + h) = a_n(t) + \dot{a}_n(t)h + \frac{h^2}{2!}\ddot{a}_n(t) + \cdots$$

$$+ \frac{h^k}{k!} a_n^k(t). \qquad (A2)$$

Since this includes higher order terms which are unknown, one may also guess all the higher terms in terms of lower order terms. The Runge–Kutta method does not use this complicated form but simplifies further and gets simple and nice looking forms,

$$a_n(t + h) \simeq a_n(t) + \tfrac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4), \qquad (A3)$$

where $k_1 = hf(a_n, t)$,

$$k_2 = hf(a_n + \tfrac{1}{2}k_1, t + \tfrac{1}{2}h),$$
$$k_3 = hf(a_n + \tfrac{1}{2}k_2, t + \tfrac{1}{2}h), \qquad (A4)$$
$$k_4 = hf(a_n + k_3, t + h).$$

Here the Taylor expansion is truncated in a fifth order. Thus the error of this method is proportional to the fifth derivative term and the convergency is excellent compared to the other methods. The advantage of this method is that the Runge–Kutta method does not require prior calculation of higher order derivatives of $a_n(t)$ as the Taylor series does, and its rapid convergence. One disadvantage is that the errors are not so easy to check. But the best way to check the errors is to monitor the value of $k_i$ how they vary. If they vary rapidly, then one may probably reduce the value of time interval $h$.

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