

NOTE

De Vogelaere's Method for the Numerical Integration of Second-Order Differential Equations without Explicit First Derivatives: Application to Coupled Equations Arising from the Schrödinger Equation¹

Many problems occur in chemistry and physics which require for their solution the numerical integration of a system of coupled second-order ordinary differential equations without first derivatives. The method of de Vogelaere [1a], [1b] has been found to be very successful [2]-[4] in certain inelastic molecular scattering problems in which coupled equations of the above general description arise. The method offers some practical advantages over more commonly used procedures.

The above scattering applications involved linear differential equations, which result from the three-dimensional Schrödinger equation, of the form [5]

$$\frac{d^2 y_i(r)}{dr^2} = \sum_{j=1}^N a_{ij}(r) y_j(r), \quad i = 1, 2, \dots, N, \quad (1)$$

where

$$a_{ij}(r) = \left(\frac{2\mu}{\hbar^2} \right) \left[\mathcal{V}_{ij}(r) - E_i \delta_{ij} + \frac{\ell_i(\ell_i + 1)\hbar^2}{2\mu r^2} \delta_{ij} \right]. \quad (2)$$

Here μ is the reduced mass of a structureless projectile-molecule system, \hbar is Planck's constant divided by 2π , $\mathcal{V}_{ij}(r)$ is a matrix element of an orientation-dependent potential energy function, $E_i (E_i > 0)$ is the energy difference between the total energy of the composite system and the molecule in the i th internal state after the collision, ℓ_i is the corresponding orbital angular momentum quantum number of the projectile in the center-of-mass coordinate system, δ_{ij} is the kronecker delta, and r is the radial coordinate. Solutions of Eqs. (1) are desired which vanish at the origin and have sinusoidal behavior for large r .

For convenience, the asymmetric potential energy function was chosen to be separable, leading to matrix elements

$$\mathcal{V}_{ij}(r) = g_{ij} V(r), \quad (3)$$

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where g_{ij} is a linear combination of angular matrix elements and $V(r)$ is the spherical part of the potential energy function. In most cases, $V(r)$ was large and positive for small r , negative for intermediate r , and approached zero for large positive r , although functions were tested that did not have the characteristic of being negative for intermediate value of r .

Eqs. (1) were integrated employing the fourth-order step-by-step method of de Vogelaere for solving

$$\frac{d^2y_i(x)}{dx^2} = F_i(x, y_1(x), y_2(x), \dots, y_N(x)), \quad i = 1, 2, \dots, N. \quad (4)$$

The purpose of this note is to call attention to this method which may have general utility for a wide class of problems.

The algorithm makes use of one intermediate point and carries out the integration from x_n to x_{n+1} by cyclic use of the equations

$$y_{i,1/2} = y_{i,0} + \frac{1}{2}hy'_{i,0} + \frac{h^2}{24}(4F_{i,0} - F_{i,-1/2}), \quad (5)$$

$$y_{i,1} = y_{i,0} + hy'_{i,0} + \frac{h^2}{6}(F_{i,0} + 2F_{i,1/2}), \quad (6)$$

$$y'_{i,1} = y'_{i,0} + \frac{h}{6}(F_{i,0} + 4F_{i,1/2} + F_{i,1}), \quad (7)$$

where

$$y_{i,s} \equiv y_i(x + sh), \quad (8)$$

$$y'_{i,s} \equiv \frac{dy_i(x + sh)}{dx}, \quad (9)$$

$$F_{i,s} \equiv F_i(x + sh, y_{1,s}, y_{2,s}, \dots, y_{N,s}), \quad (10)$$

and $h = x_{n+1} - x_n$. The integration is conveniently begun by making use of

$$y_{i,-1/2} = y_{i,0} - \frac{h}{2}y'_{i,0} + \frac{h^2}{8}F_{i,0}. \quad (11)$$

Changes of mesh, h , are easily made by replacing Eq. (5) by [1a]

$$y_{i,1/2} = y_{i,0} + \frac{h_2}{2}y'_{i,0} + \frac{h_2^2}{24} \left[\left(3 + \frac{h_2}{h_1} \right) F_{i,0} - \frac{h_2}{h_1} \bar{F}_{i,-1/2} \right], \quad (12)$$

where h_1 is the previous value of the integration mesh, h_2 is the new value, and $\bar{F}_{i,-1/2}$ denotes the value of $F_{i,-1/2}$ at $x = x_0 - h_1/2$. In addition, the algorithm

may be easily and efficiently programmed [7] following a scheme proposed by de Vogelaere [1a].

In general, the numerical integration of coupled linear second-order ordinary differential equations without explicit first derivatives dictates [8] the choice of Numerov's [9], [10] algorithm because it is the highest-order method which is at the same time a three-point method. However, the Numerov method has the disadvantage [11] of requiring separate procedures to both (a) start the integration and (b) change the mesh. (In atomic and molecular scattering applications utilizing the Numerov procedure [12], Taylor-series expansions are commonly used to obtain the necessary starting values.) These shortcomings are avoided in the present method by the use of Eqs. (11) and (12), respectively.

It is also remarked that one of the tests performed to determine the suitability of de Vogelaere's procedure for the scattering problems discussed above was a comparison with the standard fourth-order Runge-Kutta-Gill (RKG) [13] procedure for a simple problem where analytical solutions are available, namely that of two coupled harmonic oscillators (see Table I). In agreement with earlier findings for a single equation [14], the present method was found to be at least as accurate as the RKG process and to be faster than the RKG algorithm by a factor of 2.2. This result can be essentially attributed to the efficiency of de Vogelaere's algorithm which requires only two calls per step of the equation

TABLE I

$$\text{SOLUTION TO } d^2y_1(x)/dx^2 = -[(k_1 + k_3)y_1(x) + k_3y_2(x)]/m_1, \\ d^2y_2(x)/dx^2 = -[k_3y_1(x) + (k_2 + k_3)y_2(x)]/m_2,$$

WHERE $k_1 = 50$, $k_2 = 25$, $k_3 = 60$, $m_1 = 100$, AND $m_2 = 1$ FOR THE INITIAL CONDITIONS:
 $y_1(0) = 0$, $y_1'(0) = -0.88618375$, $y_2(0) = 0$, $y_2'(0) = -8.65892497$

x	ANALYTICAL SOLUTION		RUNGE-KUTTA-GILL ^a		DE VOGELAERE ^a	
	y ₁	y ₂	y ₁	y ₂	y ₁	y ₂
0.0	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000
0.5	-0.39171651	1.27961176	-0.39171659	1.27960085	-0.39171652	1.27961055
1.0	-0.73272132	0.33932142	-0.73272193	0.33923655	-0.73272156	0.33928862
1.5	-0.94955085	-0.29217546	-0.94955045	-0.29211957	-0.94955073	-0.29215881
2.0	-0.99501329	1.06599258	-0.99501218	1.06614876	-0.99501285	1.06605365
2.5	-0.88048661	1.52916784	-0.88048752	1.52903919	-0.88048691	1.52912494
3.0	-0.63274690	-0.07197542	-0.63274837	-0.07218162	-0.63274748	-0.07205724
3.5	-0.27256565	-0.61378812	-0.27256406	-0.61356425	-0.27256509	-0.61370998
4.0	0.14436873	0.56635594	0.14437035	0.56658434	0.14436938	0.56644839
4.5	0.52779987	0.31050744	0.52779749	0.31017286	0.52779902	0.31038761

^a For $h = 0.02$.

subprogram compared to four calls per step in the RKG process. No comparisons were made with the special Runge-Kutta methods appropriate when second derivatives are absent [15].

The method of de Vogelare is distinguished by its basic simplicity and elegance which results generally in less programming than other methods. This advantage coupled with the straightforward starting sequence and ease in continuously changing the integration mesh warrant the consideration of the algorithm even for coupled linear second-order differential equation with variable coefficients and missing first derivatives.

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