A reversible numerical integrator of the isokinetic equations of motion

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An explicit second-order numerical method to integrate the isokinetic equations of motion is derived by fitting circular arcs through every three consecutive points of the discretized trajectory, which is reversible and robust, and allows a good control of the variable step length. Its performance is tested by computing the thermodynamic properties of simple pair-potential models, and its chemical application is shown for the global search for stable structures, using canonical sampling and energy minimization, of hydrogen-bonded molecular clusters.

I. INTRODUCTION

Early in the history of computers, numerical methods for the atomistic simulation of thermodynamic properties of matter began their evolution\cite{1,2}. The idea of the isokinetic equations of motion seems to show up first quietly in a work\cite{3} on liquid salts, where a numerical scheme\cite{4} to solve the Newtonian equations was modified, by what was later called velocity rescaling, to keep the kinetic energy constant, the underlying differential equation, although not written out at that time, was later rediscovered\cite{5} and its properties were carefully studied\cite{6}. Optimal numerical integration of this kind of equations seems to have drawn only limited attention (which can be due in part to the shift to other deterministic thermostats\cite{7,8}), the original scheme\cite{3} lacks reversibility, the operator-splitting integrators\cite{9} were developed, 15 years later, that respect this condition. Yet 20 years later, as we took a fresh look at the problem, we saw a way to design an explicit reversible integrator of the isokinetic equations of motion based on the local circular arc interpolation — the simplest analytical curve naturally parametrized by its length, with the simplest (constant) curvature, fits well to the isokinetic trajectory and plays the same role as the parabola in the famous Verlet\cite{10} integrator. We did our best to check if this had been done before, but found nothing of the kind, so it seems to be new, and we are glad to share our findings here.

II. THEORY

The isokinetic equations of motion for a system of \( N \) atoms can be written in the form

\[
\ddot{\mathbf{r}}(t) = \left(1 - \frac{\dot{\mathbf{r}}(t) \dot{\mathbf{r}}(t) \cdot \mathbf{f}(\mathbf{r}(t))}{|\dot{\mathbf{r}}(t)|^2}\right) \mathbf{f}(\mathbf{r}(t)) \tag{1}
\]

where \( \mathbf{r}(t) \) is the 3\( N \)-dimensional vector of their cartesian coordinates as a function of time, and \( \dot{\mathbf{r}}(t) \) and \( \ddot{\mathbf{r}}(t) \) mean its first and second time derivatives. We assume unit masses of all atoms for simplicity, moreover, the masses play no role for sampling the canonical distribution in the coordinate space. The vector of forces

\[
f(\mathbf{r}) = -\frac{\partial U(\mathbf{r})}{\partial \mathbf{r}} \tag{2}
\]

can be taken as a scaled gradient of the potential energy function \( U(\mathbf{r}) \), with \( 1/\gamma = (3N - 1)T \) and \( |\mathbf{r}(t)| = 1 \) now and in the following, we get a trajectory in the configuration space \( \mathbf{r}(t) \) parametrized by its length (the now fictitious time \( t \)) with the density distribution \( \exp(-U(\mathbf{r})/T) \) in the limit \( t \to \infty \), where the temperature \( T \) is given in energy units. To start the trajectory, the positions \( \mathbf{r}(t_0) \) and the velocities \( \dot{\mathbf{r}}(t_0) \) at time \( t_0 \) are taken as input.

Numerical integration of Eq. (1) works by computing an approximate solution \( \{\mathbf{r}_n\} = \{\mathbf{r}(t_n)\} \) at discrete points in time \( \{t_n\} \), the steps \( t_{n+1} - t_n > 0 \) being small enough to get a good accuracy. A local interpolation around each point

\[
\mathbf{r}_n(t) = \mathbf{r}_n + \mathbf{c}_n(t-t_n) \tag{3}
\]

can be found that goes through the three consecutive points \( \mathbf{r}_{n-1}, \mathbf{r}_n, \) and \( \mathbf{r}_{n+1} \) at some \( t \), and making it satisfy Eq. (1) at the central point \( \mathbf{r}_n \) leads to a (generally nonlinear) dependence between the three points, so that \( \mathbf{r}_{n+1} \) is defined by \( \mathbf{r}_{n-1} \) and \( \mathbf{r}_n \), or in the same way by \( \mathbf{r}_{n-1} \) and \( \mathbf{r}_{n+1} \), thus a reversible trajectory can be computed.

In this work we propose the circular arc interpolation

\[
\mathbf{c}_n(s) = \frac{\sin(\kappa_n s)}{\kappa_n} \mathbf{z}_n + \frac{1 - \cos(\kappa_n s)}{\kappa_n^2} (1 - \mathbf{z}_n \mathbf{z}_n \cdot \mathbf{f}_n) \tag{4}
\]

with the scalar curvature

\[
\kappa_n = \sqrt{|(1 - \mathbf{z}_n \mathbf{z}_n)\mathbf{f}_n|^2 - (\mathbf{z}_n \cdot \mathbf{f}_n)^2} \tag{5}
\]

and the (unit) tangent vector \( \mathbf{z}_n \). By construction, it satisfies Eq. (1) at the central point for any unit \( \mathbf{z}_n \), but making it go through either of the two other points

\[
\mathbf{r}_{n-1} = \mathbf{r}_n + \mathbf{c}_n(-\bar{s}_n) \tag{6}
\]
\[
\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{c}_n(s_{n+1}) \tag{7}
\]
uniquely defines the tangent as either
\[ z_n = \frac{x_n + \frac{1}{2}|x_n|^2f_n}{|x_n + \frac{1}{2}|x_n|^2f_n|}, \tag{8} \]
\[ x_n \equiv r_n - r_{n-1}, \tag{9} \]
or likewise
\[ z_n = \frac{x_{n+1} - \frac{1}{2}|x_{n+1}|^2f_{n+1}}{|x_{n+1} - \frac{1}{2}|x_{n+1}|^2f_{n+1}|}. \tag{10} \]

A somewhat lengthy derivation of Eqs. (8) or (10) is given in Appendix A.

The local arc lengths \( s_n \approx \bar{s}_n \) in general are not equal,
\[ s_n = \frac{\arcsin(\kappa_{n-1} z_{n-1} \cdot x_n)}{\kappa_{n-1}}, \tag{11} \]
\[ \bar{s}_n = \frac{\arcsin(\kappa_n z_n \cdot x_n)}{\kappa_n}, \tag{12} \]
so the total path length can be computed as
\[ t_n = t_{n-1} + \frac{1}{2}(s_n + \bar{s}_n). \tag{13} \]

For a statistical average of some property \( P(\mathbf{r}) \), such as pressure,
\[ \langle P \rangle = \frac{\sum w_n P(\mathbf{r}_n)}{\sum w_n} \tag{14} \]
it seems natural to take the weights
\[ w_n = \frac{1}{2}(|\bar{s}_n| + s_{n+1}). \tag{15} \]

With all this in mind, the computation of the isokinetic trajectory starts with
\[ z_0 = \bar{r}(t_0) \tag{16} \]
and makes steps forward through Eqs. (5), (4), and (7), and also Eq. (8) for \( n > 0 \).

There is much freedom in the choice of arc lengths \( s_n \), the simplest would be to set \( s_{n+1} = \bar{s}_n \), then it can be shown that
\[ x_{n+1} = c_n(\bar{s}_n) = -(1 - 2z_n z_n^*)x_n, \tag{17} \]
thus every next step is a negative reflexion of the step before against the tangent \( \bar{s}_n \), and as such it conserves the length \( |x_{n+1}| = |x_n| = x \), a procedure elegant in its simplicity. Setting the step lengths to some values
\[ |x_{n+1}| = |c_n(s_{n+1})| = x_{n+1} \tag{18} \]
yields the arc lengths
\[ s_{n+1} = \frac{2\arcsin(\frac{1}{2}\kappa_n x_{n+1})}{\kappa_n}, \tag{19} \]
and this can be done at the first step followed by the use of Eq. (17).

For similar systems, setting the step length \( x = a\sqrt{N} \) may be meaningful, assuming each atom to move by \( \sim a \) on every step, but hot atoms can show up, from time to time, moving by up to \( a\sqrt{N} \), which can become dangerous for large \( N \). We think a more mindful step size control would be to limit the atomic moves
\[ \max |x_{i,n+1}| = \max i \min |c_{i,n}(s_{n+1})| = a, \tag{20} \]
where \( i \) labels the \( i \)-th atom’s components of vectors, and also to limit the bend angle
\[ \kappa_n s_{n+1} \leq \alpha, \tag{21} \]
the solution being
\[ s_{n+1} = \frac{1}{\kappa_n} \min \left( \min_i \theta_{i,n+1}, \alpha \right) \tag{22} \]
where the atomic values \( \theta_{i,n+1} \) are the smallest roots
\[ p \left( \theta_{i,n+1}, \frac{|z_{in}|^2}{\kappa_n^2 a^2}, \frac{z_{in} \cdot y_{in}}{\kappa_n^2 a^2}, \frac{|y_{in}|^2}{\kappa_n^2 a^2} \right) = 0, \tag{23} \]
\[ y_n \equiv (1 - z_n z_n^*)f_n, \tag{24} \]
of the functions
\[ p(\theta, u, w, v) = u \sin^2 \theta + 2w(1 - \cos \theta) \sin \theta + v(1 - \cos \theta)^2 - 1, \tag{25} \]
or \( \theta_{i,n+1} = \pi \) if there are no roots for some \( i \). Finding the roots \( \theta \) of functions (25) works through the solution of a quartic equation as detailed in Appendix B. Care should be taken if \( \kappa_n \) is small (our threshold is \( \kappa_n < 2^{-12} \)), then the trigonometric functions can be expanded in powers around zero, and with \( \theta_{i,n+1} = \kappa_n s_{i,n+1} \) Eq. (23) is replaced by
\[ q(s_{i,n+1}, \frac{|z_{in}|^2}{a^2}, \frac{z_{in} \cdot y_{in}}{a^2}, \frac{|y_{in}|^2}{4a^2} - \frac{\kappa_n^2 |z_{in}|^2}{3a^2}) = 0, \tag{26} \]
the roots \( s_{i,n+1} \) now being of the quartic function
\[ q(s, u, w, v) = us^2 + ws^3 + vs^4 - 1, \tag{27} \]
finding them in a stable way needs some further tricks as also explained at the end of Appendix B.

When solving \( N \) Eqs (23) or (26) on every step seems too heavy, an approximation
\[ s_{n+1} = \min \left( \frac{a}{\max |z_{in}|}, \frac{\alpha}{\kappa_n} \right) \tag{28} \]
can be used instead of Eq. (22), which does not respect Eq. (20) exactly but does limit the atomic moves in some way.
If the infinitesimal translations and rotations of the whole system have to be removed from the trajectory (or some other constraints enforced), the tangents can be projected

$$z_n^o = O_n z_n$$

(29)

by the well-known matrices $O_n$ at each point, and then not only $z_n$ in Eq. (4) should be replaced with $z_n^o$, but also

$$f_n^o = -2 \frac{x_n}{|x_n|^2}$$

(30)

should be substituted for $f_n$, the latter follows from Eq. (A17) in Appendix A

A retrospective error estimate

$$\varepsilon_n = |r_n(t_n - 2) - r_n - 2|$$

(31)

and its mean ($\bar{\varepsilon}$) and largest $\varepsilon_{\text{max}}$ values over the trajectory can be easily computed and used to judge the local accuracy of the integrator.

III. NUMERICAL TESTS

We test our numerical integrator on finite atomic or molecular systems inside a spherical vessel of volume $V$, adding a term

$$U_0(r, V) = \sum_i u_0 \left( |r_i| - \frac{3V}{4\pi} \right),$$

(32)

to the potential energy, with a particle-wall interaction

$$u_0(r) = \begin{cases} 
0, & r \leq 0 \\
\frac{1}{2} c b r^2/(b - r), & 0 < r < b \\n\infty, & r \geq b 
\end{cases}$$

(33)

which allows the pressure to be computed as the average of the volume derivative

$$P(r) = -\frac{\partial U_0(r, V)}{\partial V}$$

(34)

over the trajectory as in Eq. (14). In the limit $b \to \infty$ Eq. (33) is simply a switched harmonic potential with force constant $c$, a finite $b$ will keep all atoms from getting deeper than $b$ into the elastic wall. For the ideal gas inside such a non-ideal vessel, the partition function and the pressure can be computed analytically for $b = \infty$, thus the fugacity factor

$$\varphi = \frac{PV}{NT} = \frac{1 + \sqrt{\frac{\pi}{3} \mu + \mu^2}}{1 + \frac{3}{2} \sqrt{\frac{\pi}{3} \mu + 3\mu^2} + \frac{3}{4} \sqrt{\frac{\pi}{3} \mu^3}}$$

(35)

with

$$\mu = \frac{\sqrt{2T}}{c} \cdot 3 \sqrt{\frac{4\pi}{3V}}$$

(36)

| $V/N$ | $\varphi$ | $\varphi^\circ$ | $\varphi^\text{walk}$ | $\varphi^\text{ideal}$ |
|-------|--------|-----------|----------------|-----------------|
| 1     | 0.8907 | 0.8842    | 0.8845          | 0.8861          |
| 2     | 0.8861 | 0.8890    | 0.8903          | 0.8906          |
| 4     | 0.9076 | 0.9099    | 0.9102          | 0.9110          |
| 8     | 0.9295 | 0.9275    | 0.9277          | 0.9281          |
| 16    | 0.9411 | 0.9419    | 0.9422          | 0.9422          |
| 32    | 0.9538 | 0.9540    | 0.9546          | 0.9543          |
| 64    | 0.9642 | 0.9635    | 0.9636          | 0.9629          |
| 128   | 0.9728 | 0.9713    | 0.9713          | 0.9704          |
| 256   | 0.9798 | 0.9776    | 0.9776          | 0.9763          |
| 512   | 0.9855 | 0.9827    | 0.9826          | 0.9812          |
| 1024  | 0.9901 | 0.9868    | 0.9865          | 0.9851          |
| 2048  | 0.9940 | 0.9899    | 0.9898          | 0.9882          |
| 4096  | 0.9970 | 0.9924    | 0.9927          | 0.9909          |
| 8192  | 0.9995 | 0.9945    | 0.9946          | 0.9923          |

The wall potential has $c = 256$ and $b = \infty$, the atomic step size $a$ as is in Eq. (29), the number of sampling $n$ and burn-in $n_0$ steps is shown, the mean ($\bar{\varepsilon}$) and largest $\varepsilon_{\text{max}}$ local errors are from Eq. (11), and $\langle \alpha \rangle$ is the mean bend angle $\alpha_n = \kappa_n s_{n+1}$. The values $\varphi_{\text{walk}}$ are from the random walk integration, $\varphi_{\text{ideal}}$ are from Eq. (29).

In the numerical computation of the isokinetic trajectory, the projection of rotations (but not translations) of the whole system in Eq. (29) is helpful, and we do it throughout this work.

A model system of atoms with only pairwise interactions

$$U_2(r) = \sum_{i<j} u(|r_i - r_j|)$$

(37)

with either the purely repulsive potential of Hertzian spheres

$$u(r) = \begin{cases} 
(1 - r)^{5/2}, & r < 1 \\
0, & r \geq 1 
\end{cases}$$

(38)

or the more realistic Lennard-Jones potential

$$u(r) = r^{12} - 2r^6$$

(39)

should be good enough for testing the properties of the numerical integrator.

Table I shows our results for the hot nearly-ideal few-atom gas of Hertzian spheres. The cubic scaling of the local errors ($\bar{\varepsilon}$) and $\varepsilon_{\text{max}}$ with the step size $a$ is a clear witness of the second-order numerical accuracy of the integrator. We have also run the random walk integrations and the pressures (see $\varphi_{\text{walk}}$ in Table I) match those from our isokinetic trajectory to within the statistical errors, which we estimate by the blocking method. Even though there are $3N - 3$ degrees of freedom (as the rotations of the whole are zeroed out), there still must be the factor of $3N - 1$ in the definition of $\gamma$ in Eq. (2) — thanks to this few-atom example we have learned this truth, should we have played with many atoms from the very beginning, we would have likely overlooked it.
TABLE II. Computation on N = 201 Lennard-Jones atoms.

| α   | 1/16 | 1/32 | 1/64 |
|-----|------|------|------|
| n_0 | n_0  | n_0  | n_0  |
| Δt  | Δt^2 | Δt^2 | Δt^2 |
| ε   | ε   | ε   | ε   |

The spherical vessel volume V/N = 64, c = 256, b = 1.

Fugacity factor ϕ, mean local integration error (ε) and bend angle (α).

αPhase state: (s) solid, (l) liquid, (g) gas.

A more characteristic example of thermodynamic integration is shown in Table II where N = 201 Lennard-Jones atoms in volume V/N = 64 form solid, liquid, and gas phases in a range of temperatures.

IV. CHEMICAL APPLICATIONS

Automated global searches for stationary points on molecular potential energy surfaces can be a very helpful tool for theoretical chemists, as their chemical intuition alone can not always find all the ways in which the atoms can bind together. Points on the isokinetic trajectory, at a good distance between them, can be taken as the input to energy minimization (or saddle point optimization), and the optimized points can then be sieved to remove duplicates and thus to find a set of unique structures that may be further sorted by their energies. To get the most out of it for a given amount of computer time, a meaningful setting of the key parameters is needed: the temperature T should be neither too low (to overcome the barriers sooner) nor too high (to keep the bonds broken), the volume V neither too small (to give some freedom of motion) nor too high (to hold the whole together), the distance between the points taken from the trajectory neither too short (to get new structures most of the time) nor too long (to keep from wasting time), and the integration step size can now be greater but not too much.

Here we report our first experience with such global search technique on the example of a few hydrogen-bonded molecular clusters, their potential energy surfaces being computed by our parametrizable electronic structure models. First of all, we took two typical temperatures — 0.001 au (316 K) and 0.002 au (632 K) — and sought, on a power-of-two scale, the best atomic step size, finding Δt = 2^(-32) au to be rather good for any molecules, with ε_{max} < 0.01 au. Next, we have tailored the other settings for the best hit rate of the global searches, as shown in Table III. On the water dodecamer (H_2O)_{12} the distance l in steps between the to-be-optimized trajectory points was adjusted to bring nearly the lowest cost of finding a new structure measured as (l + ⟨k⟩)M/m, where ⟨k⟩ is the mean number of steps of a BFGS-based energy minimization procedure, M is the number of optimized structures, m of which are unique, so l = 128 is a good choice for both temperatures. Doubling the volume to V/N = 256 au raises the cost through greater ⟨k⟩, more so for the higher T, so we take it only in the cold case, and with these settings we study all other molecular clusters. A weak dependence of ⟨k⟩ on the system size is seen. For the smaller systems, most if not all of the stable structures seem to be found, and the global minimum is likely to be amoung them. We cannot help showing one such least-energy structure in Figure 1 as an illustration to the Chemist of how this pure mathematics opens a window to the wonderful world of wet chemistry.

FIG. 1. The lowest-energy structure of alanine and six water molecules Ala(H_2O)_6, as found by the calculations.
V. CONCLUSIONS

The new reversible second-order numerical integration scheme for the isokinetic equations of motion derived here based on the circular-arc interpolation has an elegant simplicity of its formulas and works well with the potential functions typical of molecular systems.

Appendix A: The tangent equation

To find \( z \), such that \(|z| = 1\), from the equation
\[
\frac{\sin(\kappa s)}{\kappa}z + \frac{1 - \cos(\kappa s)}{\kappa^2}(1 - zz)f = -x
\]  
(A1)

with
\[
\kappa = |(1 - zz)f| = \sqrt{|f|^2 - (z \cdot f)^2}
\]  
(A2)

for given \( f \) and \( x \), the dot product of both sides with \( z \) is taken first, hence
\[
\frac{\sin(\kappa s)}{\kappa} = -z \cdot x
\]  
(A3)

from which, by the way, Eqs. (11) and (12) follow. Now \( \sin(\kappa s) \) and \( \cos(\kappa s) \) in terms of \( z \cdot x \) are put back into Eq. (A1) to get
\[
- zz \cdot x + y(1 - zz)f = -x
\]  
(A4)

and if rewritten as the projection
\[
(1 - zz)(x + yf) = 0,
\]  
(A5)

it becomes clear that
\[
z = \frac{x + yf}{|x + yf|},
\]  
(A6)

and only \( y \) is yet to be found.

To simplify further notations,
\[
\chi = |x|^2, \quad \phi = |f|^2, \quad \psi = x \cdot f,
\]  
(A7)

then from Eqs. (A2) and (A7) follows
\[
k^2 = \phi - \frac{(\psi + y\phi)^2}{\chi + 2y\psi + y^2\phi} = \frac{\chi \phi - \psi^2}{\chi + 2y\psi + y^2\phi},
\]  
(A8)

putting it together with
\[
(z \cdot x)^2 = \frac{(\chi + y\psi)^2}{\chi + 2y\psi + y^2\phi}
\]  
(A9)

into Eq. (A5) yields
\[
\sqrt{1 - \frac{(\chi\phi - \psi^2)(\chi + y\psi)^2}{(\chi + 2y\psi + y^2\phi)^2}} = \frac{1 - (\chi\phi - \psi^2)y}{\chi + 2y\psi + y^2\phi},
\]  
(A10)

multiplying both sides with \( \chi + 2y\psi + y^2\phi \) followed by squaring, gathering the terms, and dividing by \( \chi\phi - \psi^2 \) leads to
\[
2(\chi + 2y\psi + y^2\phi)y - (\chi\phi - \psi^2)y^2 - (\chi + y\psi)^2 = 0
\]  
(A11)

and at last to the cubic equation
\[
2\phi y^3 + (4\psi - \chi\phi)y^2 + 2\chi(1 - y) - \chi^2 = 0
\]  
(A12)

looking at which we see (wow!) that it always (for any \( \phi \) and \( \psi \)) has the root \( y = \frac{1}{\chi} \), and this is the only real root, except the unlikely special case \( \psi = \chi\phi \) of no interest, as can be shown by rewriting the cubic equation as
\[
(2y - \chi)(\phi y^2 + 2\psi y + \chi) = 0
\]  
(A13)

and knowing the inequality \( \psi^2 \leq \chi\phi \), thus the answer is
\[
z = \frac{x + \frac{1}{\chi}|x|^2 f}{|x + \frac{1}{\chi}|x|^2 f|}
\]  
(A14)

Finding \( f \) for given \( x \) and \( z \) leads to
\[
f = 2\frac{uz - x}{|x|^2}
\]  
(A15)

with arbitrary \( u \), but if this \( f \) is then needed in projected form (1 - \( zz \))\( f \) as in Eq. (A4), then \( u = 0 \) is a natural choice, and
\[
f = -2\frac{x}{|x|^2}
\]  
(A16)

Appendix B: The step length equation

To solve the equation
\[
u \sin^2 \theta + 2w(1 - \cos \theta) \sin \theta + v(1 - \cos \theta)^2 = 1,
\]  
(B1)

a change to variable
\[
s = \sin^2 \left( \frac{1}{2} \theta \right)
\]  
(B2)

makes
\[
4us(1 - s) + 8w\sqrt{s - s^2} + 4vs^2 = 1,
\]  
(B3)

moving the terms to leave the square root alone on the left hand side, then taking the square of both sides,
\[
64w^2(s^3 - s^4) = (1 - 4us + 4(u - v)s^2)^2,
\]  
(B4)

and gathering the powers of \( s \) yields the quartic equation
\[
1 - 8us + 8(u - v + 2w^2)s^2 - 32(u(u - v) + 2w^2)s^3 + 16((u - v)^2 + 4w^2)s^4 = 0.
\]  
(B5)
then a change of variable

\[ x = \frac{1}{u + v} \left( \frac{1}{s} - 2u \right) = \frac{1}{u + v} \left( \frac{1}{\sin^2 \left( \frac{s}{2} \right)} - 2u \right) \quad (B6) \]

leads to the well-behaved depressed quartic equation

\[
\begin{align*}
& x^4 + 8 \frac{u - v - u^2}{(u + v)^2} x^2 - 64 \frac{w^2}{(u + v)^3} x \\
& + 16 \left( u - v - u^2 \right)^2 + 4 \left( 8u^2 \right) w^2 (u + v)^4 = 0
\end{align*}
\]

(B7)

that can be stably solved by the classic 16th–18th century methods on modern hardware.

The quartic equation

\[ us^2 + w^3 s + v^4 s = 1 \quad (B8) \]

that comes from Eq. (20) needs careful handling when \( w \ll u^{3/2} \) and \( v \ll u^2 \), which often happens. With a good threshold value \( \eta \approx 2^{-10} \), if

\[ w > \eta u^{3/2} \quad \text{or} \quad v > \eta u^2, \]

then a change of variable

\[ s = \frac{h}{x}, \quad (B10) \]

\[ h = \frac{1}{\sqrt{u^* + v}} \quad (B11) \]

yields a well-behaved depressed quartic equation

\[ x^4 - h^2 u x^2 - h^3 w x - h^4 v = 0 \quad (B12) \]

that can be solved by standard means with some care taken to gather the terms in the determinant of its resolvent cubic equation. Otherwise, the change of variable

\[ s = \frac{1}{\xi \sqrt{u}} \quad (B13) \]

leads to

\[ \xi^4 - \xi^2 - \gamma \xi - \nu = 0, \quad (B14) \]

with

\[ \gamma = \frac{w}{u^{3/2}}, \quad \nu = \frac{v}{u^2}, \quad (B15) \]

and now the function \( \xi(\gamma, \nu) \) is expanded in powers of its arguments by perturbation theory,

\[ \xi = 1 + \frac{1}{2} \gamma + \frac{1}{2} \nu - \frac{3}{8} \gamma^2 - \gamma \nu - \frac{5}{8} \nu^2 + \frac{1}{2} \gamma^3 + \ldots, \quad (B16) \]

the terms up to \( \gamma^3 \), as written, are enough to get a good accuracy.

Last but not least, the identity \( 1 - \cos \theta = 2 \sin^2 \left( \frac{1}{2\theta} \right) \) should be used for a stable evaluation of \( 1 - \cos \theta \) everywhere (as in Eq. (41)) in numerical computations.

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