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A Numerical Method for Calculation of Phase Shifts

S. Bosanac

Theoretical Chemistry Group, Ruđer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

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A method for calculating the phase shifts is described. The main idea is to transform Schrödinger equation to an equivalent, nonlinear form, the solution of which is not oscillatory in the first order. Therefore, the equation is easy to be solved numerically.

INTRODUCTION

The radial Schrödinger equation for a two atom system is

$$\psi'' = (V(r) + \frac{l(l+1)}{r^2} - k^2)\psi = f(r)\psi \tag{1.1}$$

where $V(r)$ is a two atom interaction potential. It has a short range repulsive part, a deep well and the tail is asymptotically as r^{-6} and represents the induced dipole-dipole interaction. The physically important solution of (1.1), is regular at the origin i. e. it goes to zero as r^{l+1}.

Solving (1.1) can be a difficult problem, especially for the waves of a short wave length. In such cases the best known analytic but approximate solution of (1.1) is provided by the WKB method[1]. This method gives rather good results but it fails when applied to problems where the turning points of $f(r)$ are not well separated. Therefore, there is still a need for a reliable, stable and fast numerical method for solving (1.1) exactly, which can then be used as a reference for the approximate ones.

One can use a number of numerical procedures for solving (1.1), the best known being the Cooly-Numerov[2], Runge-Kutta[3] methods and their modifications. There are quite sophisticated computer packages developed for solving differential equations[4]. One can also use a semianalytic method[5] which approximates $f(r)$ by a series of straight lines, and then joins the analytic solution of each step to an overall smooth solution of (1.1). This method, although independant of the oscillations of ψ, is still hampered by the fact that $f(r)$ is approximated by a combination of straight lines. The just mentioned methods become either unstable, slow or inaccurate when ψ is rapidly oscillating.

Here we start by asking whether a direct solution of (1.1) is realy necessary for getting meaningful results. For example, it will be shown that in calculating the phase shifts (therefore the scattering amplitude, hence the cross section) we require the logarithmic derivative of ψ rather then the wave function explicitly. Starting from this, we will obtain an equation equivalent

to the Schrödinger equation, the solution of which is not oscillatory. However, the resulting equation is not linear. A comparison with a similar method of Calogero[6] will be made in the Conclusion.

Let us suppose that the wave function ψ was integrated from the origin to $r = r_{\max}$ where the potential $V(r)$ is practically zero. The resulting form of (1.1) is

$$\psi_0'' = \left(\frac{l(l+1)}{r^2} - k^2 \right) \psi_0 \tag{1.2}$$

the solutions of which are the Hankel functions[7]

$$\psi_0 = \sqrt{kr}\, H_\lambda^{(1),(2)}(kr)$$

where $\lambda = l + 1/2$. Therefore, we put at $r = r_{\max}$

$$\psi = \sqrt{kr}\,(\mathrm{a}\, H_\lambda^{(1)}(kr) + \mathrm{b}\, H_\lambda^{(2)}(kr)) \tag{1.3}$$

$$\psi'(r) = \frac{1}{2r}\psi + k\sqrt{kr}\,(\mathrm{a}\, H_\lambda^{(1)'}(kr) + \mathrm{b}\, H_\lambda^{(2)'}(kr)$$

The set of equations (1.3) determines coefficients a and b.
Asymptotically the Hankel functions behave as plane waves[7]

$$\sqrt{kr}\, H_\lambda^{(1),(2)}(kr) \sim \exp\left(\pm \mathrm{i}\left(kr - \frac{\lambda}{2}\pi - \frac{\pi}{4}\right)\right) \tag{1.4}$$

so that ψ becomes for $r \to \infty$

$$\psi \sim \mathrm{a}\exp\left(\mathrm{i}\left(kr - \frac{\pi}{2}\left(\lambda + \frac{1}{2}\right)\right)\right) + \mathrm{b}\exp\left(-\mathrm{i}\left(kr - \frac{\pi}{2}\left(\lambda + \frac{1}{2}\right)\right)\right) \tag{1.5}$$

Since the phase shift is defined as[8]

$$\psi \sim \sin\left(kr - \frac{1}{2}l\pi + \delta_l\right) \tag{1.6}$$

or the **S**-matrix by

$$\mathbf{S} = \mathbf{S}(\lambda, k) = \exp(2\mathrm{i}\,\delta_l) = \frac{\mathrm{a}}{\mathrm{b}} \tag{1.7}$$

the absolute values of coefficients a and b are immaterial. Only their relative phase is essential. Hence, coefficients a and b are arbitrary up to a common constant. In this way the set of equations (1.3) is solved for the ratio a/b. Using the recurrence relation for the Bessel functions[7], we get

$$\frac{\mathrm{a}}{\mathrm{b}} = -\frac{\left(\frac{X}{k} - \frac{1}{2z} + \frac{\lambda}{z}\right) H_\lambda^{(2)}(z) - H_{\lambda-1}^{(2)}(z)}{\left(\frac{X}{k} - \frac{1}{2z} + \frac{\lambda}{z}\right) H_\lambda^{(1)}(z) - H_{\lambda-1}^{(1)}(z)} \tag{1.8}$$

where $X = \psi'/\psi$ and $z = kr_{\max}$. It follows that for a complete determination of the phase shifts we require X, the logarithmic derivative of the wave function.

NUMERICAL PROCEDURE

Let us find the equation satisfied by the function X. By taking derivative of X and using (1.1) we obtain

$$X' = f - X^2 \tag{2.1}$$

which is a first order nonlinear equation. Solving (2.1) when $f > 0$ presents no problem since ψ and hence ψ' is a monotonically varying function. However, the exception is when $\psi = 0$ in which case the function X is infinite. Therefore, we define, near that point, another function $Y = 1/X$, which is not singular there. The equation for Y is

$$Y' = 1 - f\,Y^2 \tag{2.2}$$

The suggested procedure alternately using (2.1) and (2.2) to obtain the solution X works well when integrating in the tunneling region. However, in the oscillatory region the method becomes even more cumbersome then direct numerical integration of (1.1), because the points where $\psi = 0$ are very closely spaced.

The main source of the oscillations of ψ (hence X) is the large negative value of f. The solution of (1.1), in that case, is approximately sin and cos with the argument $\sqrt{|f|}\,r$. Therefore we put

$$Y = \frac{1}{\sqrt{f}} \tanh(\sqrt{f}\,Z) \tag{2.3}$$

being the exact solution of (2.2) if f is constant. The equation for Z is now obtained if we let f be r dependant. Taking derivative of Y and using (2.2) we get

$$Z' = 1 + \frac{f'}{2f}\left(\frac{\sinh(2\sqrt{f}\,Z)}{2\sqrt{f}} - Z\right) \tag{2.4}$$

Let us discusse the last equation. When f is large and negative i. e. in the highly oscillatory region, sinh is with the imaginary argument, therefore it is by the modulus less then one. Since Z can be a large number, it follows that the equation (2.4) reduces

$$Z' = 1 - \frac{f'}{2f} Z \tag{2.5}$$

the solution of which is non oscillatory. Therefore, the equation (2.4) has a solution which is in the first order a monotonic function. We can estimate the contribution of the oscillatory term. For that purpose, let us define a new variable

$$U = \sqrt{f}\,Z \tag{2.6}$$

and the equation it satisfies is

$$U' = \sqrt{f} + \frac{f'}{4f} \sinh(2U) \tag{2.7}$$

or if we define $g = -f$ and $U \to iU$

$$U' = \sqrt{g} + \frac{g'}{4g} \sin(2U) \tag{2.8}$$

Since the ratio g'/g is small, the zero-th order solution of (2.8) is

$$U_0 = \int_{r_0}^{r} \sqrt{g}\, dr' = \sqrt{f}\, Z_0 \tag{2.9}$$

which is also the solution of (2.5). The difference $U - U_0$ is small and oscillatory and let us designate it by e. The value of e is a measure of the numerical procedure stability.

Let us replace U by $U_0 + e$ in (2.8). Assuming that e is small, we obtaine an equation for e

$$e' = \frac{g'}{4g}\,(e\,\cos(2U_0) + \sin(2U_0)) \tag{2.10}$$

having the analytic solution

$$e = \frac{1}{4}\int_{r_0}^{r} dr'\,\frac{g'}{g}\,\sin(2U_0)\,\exp\left(\frac{1}{2}\int_{r'}^{r}\frac{g'}{g}\cos(2U_0)\,dr''\right) \tag{2.11}$$

Therefore, the approximate solution of (2.8) to the order e^2 is

$$U = U_0 + e + C \tag{2.12}$$

where U_0 is given by (2.9) and e by (2.11). The constant C is determined from the initial condition at $r = r_0$.

Since the ratio g'/g is small and $\sin(2\,U_0)$ rapidly oscillating, e is indeed negligible. Therefore integrating (2.8) is no problem because the most dominant solution is nonoscillatory.

However, the procedure fails when g changes sign. In that case, we go back to the equations (2.1) and (2.2) and integrate these through the tunneling region. When coming out again to the oscillatory side, we use the inverse of (2.3)

$$Z = \frac{1}{2\sqrt{f}}\,\ln\frac{1+\sqrt{f}\,Y}{1-\sqrt{f}\,Y} \tag{2.13}$$

and continue integrating Z.

There is an exception. Integrating (2.4) through the first turning point i. e. when going from the origin to the attractive part of the potential, does not fail when $f(g)$ changes sign. The reason why this does not happen will now be explained.

Let us firstly prove that Z is positive and small in the tunneling region of the repulsive part of potential. Let us assume contrary i. e. $Z \gg 1$. Then the product $\sqrt{f}\,Z$ is real and large, therefore

$$U' \approx \frac{f'}{2f}\,\exp(2U) \tag{2.14}$$

with the solution which decays off fast since f' is negative. Therefore, U is damped whenever reaching such values that

$$\left|\frac{f'}{8f}\,\exp(2U)\right| > \sqrt{f} \tag{2.15}$$

and is increasing for

$$\left| \frac{f'}{8f} \exp(2U) \right| < \sqrt{f} \tag{2.16}$$

since f is positive. Hence, the solution U is somewhere in the middle i. e. U satisfies the equation

$$-\frac{f'}{8f} \exp(2U) \sim \sqrt{f} \tag{2.17}$$

and the solution is

$$Z \sim \frac{1}{2\sqrt{f}} \ln\left(-\frac{8f\sqrt{f}}{f'}\right) \tag{2.18}$$

being positive and small when f is large.

When r approaches the turning point, Z stays small and the product $\sqrt{f}Z$ goes to zero. The argument being small near the turning point, sinh can be approximated by the first two terms in the power series expansion. The leading term will then cancel with Z and the derivative Z' at the turning point is finite. Therefore, integrating the equation (2.4) through the first turning point is accomplished without any difficulty.

In conclusion we may say that the suggested numerical procedure is applied without any restriction in the tunneling, oscillatory and transition region. However, when going from the oscillatory into the tunneling side of $f(r)$, equations (2.1) and (2.2) should be applied.

CALCULATION OF THE S-MATRIX

The **S**-matrix is defined by (1.7) and (1.8). We can transform (1.8) into a form which is less sophisticated but is approximate. Therefore we write (2.3) in an equivalent form

$$\frac{1}{Y} = \sqrt{f} + \sqrt{f}\,\frac{1 - i\tan(\sqrt{|f|}\,Z)}{i\tan(\sqrt{|f|}\,Z)} \tag{3.1}$$

We also notice that the ratio $H^{(1)}_{\lambda-1}(z)/H^{(1)'}_{\lambda}(z)$ is approximately[10]

$$\frac{H^{(1)}_{\lambda-1}(z)}{H^{(1)}_{\lambda}(z)} \sim \frac{\lambda}{z} - \frac{1}{2z} + \sqrt{\frac{\lambda^2 - \frac{1}{4}}{z^2} - 1} \tag{3.2}$$

which is deduced from the asymptotic expansion of the Hankel functions. Therefore, we write

$$\mathbf{S}(\lambda, k) \sim -\frac{H^{(2)}_{\lambda}(z)}{H^{(1)}_{\lambda}(z)}\,\frac{1 - i\tan(\sqrt{|f|}\,Z)}{1 - i\tan(\sqrt{|f|}\,Z)} \tag{3.3}$$

where we have used an approximate relationship

$$\frac{H^{(2)}_{\lambda-1}(z)}{H^{(2)}_{\lambda}(z)} \sim \frac{\lambda}{z} - \frac{1}{2z} - \sqrt{\frac{\lambda^2 - \frac{1}{4}}{z^2} - 1} \tag{3.4}$$

Therefore, we have

$$\mathbf{S}(\lambda, k) \sim -\frac{H^{(2)}_{\lambda}(z)}{H^{\lambda}_{(1)}(z)} \exp(2i\sqrt{|f|\ Z}) \tag{3.5}$$

Before showing by an example how the method works, let us define the potential we are going to use.

Strictly speaking, we start integrating from $r = 0$ and finish at $r = \infty$. However, in practice this never happens. Since the approximation (2.18) works well near the origin, it is no use to integrate the solution we know. Furthermore, (2.18) is independent of the initial value of Z. However there is such a point $r = r_{\min}$, where when Z is calculated for $r > r_{\min}$, the solution will depend on the initial condition taken at $r = r_{\min}$. This point is usually where the tunneling becomes significant. Therefore, we define the potential at $r = r_{\min}$ to be infinite and set the wave function, hence Z, strictly to zero. Such definition of $V(r)$ does not alter the value of the **S**-matrix since the perturbation introduced into the wave function caused by setting its value to zero at $r = r_{\min}$, is of the order of tunneling. If $r_{\min}$ is determined for $l = 0$ and kept constant for $l > 0$, the perturbation will be even smaller because higher angular momentum introduces more repulsion.

For large r, the potential $V(r)$ goes to zero faster then the centrifugal term. Therefore, for r greater then some $r_{\max}$, the potential is small compared to $l(l+1)/r^2 - k^2$ and can easily be set to zero. That introduces yet another perturbation to the wave function, hence to the **S**-matrix, which is of the order

$$\varepsilon = |V(r_{\max})| / k^2 \tag{3.6}$$

This follows from the distorted Born expansion[8] of the wave function. If ε is small, the difference between the exact result and the approximate **S**-matrix, will be negligible.

Finally, the realistic potential that we use in the calculation is defined as

$$V(r) = \begin{cases} \infty & : r < r_{\min} \\ V(r) & : r_{\min} \leqslant r \leqslant r_{\max} \\ 0 & : r > r_{\max} \end{cases} \tag{3.7}$$

where $r_{\min}$ and $r_{\max}$ are constant for all l. It is important to notice that this form of potential does not significantly change the value of the cross section.

Although the definition (3.7) seems self evident, the application forces us to insist on the form (3.7) rather then on the exact potential. Only seldom the full length of $V(r)$ is used i. e. $r_{\min} = 0$ and $r_{\max} = \infty$ are taken.

The exact results for the **S**-matrix and those calculated by using (2.4) are compared with the WKB solution. If there is only one turning point of $f(r)$, the **S**-matrix in the WKB approximation is[9]

$$\mathbf{S}(\lambda, k) = \exp\left(i\left(\pi(l + 1/2) + 2\int_a^{\infty}(\sqrt{f} - k)\,dr - 2ka\right)\right) \tag{3.8}$$

the turning point being a. We will use the approximate result (3.8) to compare with the formula (3.5).

CALCULATION ON A MODEL POTENTIAL

We illustrate how the method works for a model potential

$$V = V_0 \exp(-a(r - r_0))(\exp(-a(r - r_0)) - 2) \tag{4.1}$$

where the parameters are $V_0 = 1136$ Å^{-2}, $a = 2.4$ Å^{-1} and $r_0 = 0.74$ Å. The energy at which the calculation is done was $k^2 = 25$ Å^{-2}. The parameters for (4.1) are roughly that of H + H system. The reason why such a system is chosen can be easily explained. For heavier atoms one expects the method to work better since the module of f is large and e as defined in (2.11) is small. Therefore, the numerical procedure is more stable. Hydrogen atoms, being the lightest representatives, are the most severe test for the method.

Let us firstly fix the parameters r_{min} and r_{max}. One can use the WKB method to estimate the tunneling near the origin and decide on r_{min}. The value $r_{min} = 0.2$ Å was taken and the estimated tunneling for ψ is of the order 10^{-8}. Similarly, $r_{max} = 8$ Å gives the value 10^{-6} for the ratio (3.6).

Our first task is to calculate e and to estimate the accuracy of the final result. Figure 1. shows results of the calculation for $l = 16$. This angular momentum produces f with a small negative value around $r = 3$ Å.

The doted line in the same Figure represents f and was inserted to relate e to f. In such a way, we gain more insight into the qualitative behaviour of e. The calculation was done with two different initial values of r.

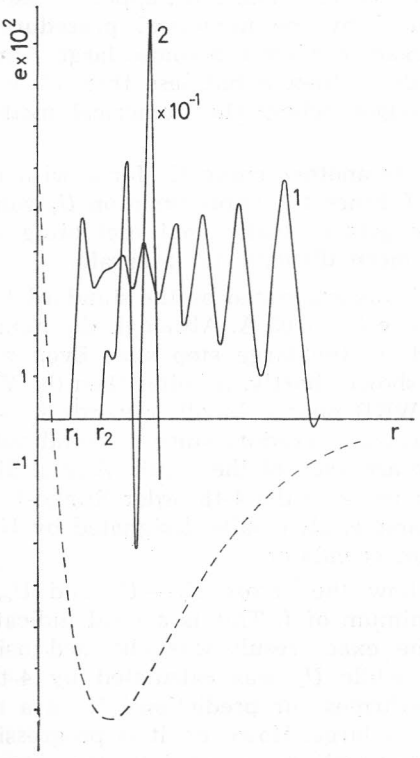

Figure 1. Behaviour of e (given by (2.11)) for two different values of r_0. The broken line represents $f(r)$.

Let us suppose that we have successfully integrated Z to the point $r = r_1$ and the result is exact. At that point we decide to use another less accurate numerical procedure which cannot follow the rapid oscillations. Then e (curve 1), with the initial condition $e = 0$ at $r = r_1$ is showing the error of our method once we get out of the oscillatory region. e was calculated from (2.11). It should be stressed that e is not a cumulative error i. e. it is the absolute error at one particular point. Secondly, it is the error absolute in character and therefore independent of the value U_0. This fact is of a considerable help because the value of U_0 can be quite large and since for the **S**-matrix we are taking the sin and cos of U, all the significant digits in front of the decimal point are disregarded. It is therefore a comfortable thought to know that what we are left with is accurate to within the error e.

The curve representing e shows that the exact U is given by

$$U_{\text{exact}}(R) = U_0(R) + e(R) + \Theta(\max(e^2)) + C$$

where $\max(e^2)$ is the maximum value of e^2 from the interval $r_1 < r < R$. The error e oscillates around the value 3.5×10^{-2}, but the amplitude gets larger. However, this should not bother us since we integrate the equation for Z and the solution roughly follows Z_0. Whenever the error e becomes large, the numerical procedure takes this into account. Such contributions average out and the numerical procedure takes some mean value for e until the error e becomes very large. However, when this happens, e oscillates with reasonable frequency easily handled by the numerical procedure. In other words, Z_0 goes smoothly to the exact Z when e becomes large. Final result for **S**-matrix is therefore more accurate then e but less then e^2, where e is an average value of e from the region where the numerical method cannot follow the oscillations.

In Figure 1. there is another curve (2) for e with initial condition taken near the minimum of f. Since the approximation U_0 works better then in the previous example, one gets e smaller but oscillating with relatively larger amplitudes, therefore more difficult to integrate.

The equation for Z was integrated by the standard 4-th order Runge-Kutta method with the step size $h = 0.05$ Å. Although the numerical method is quite stable, it is hampered by the large step size. Even so the final result for **S**-matrix, as it will be shown shortly, is better then the WKB result (one should notice that U_0 is the WKB phase). In other words it is not necessary to use any sophisticated numerical procedure since it would automatically take small step size to ensure the accuracy of the result. Any straightforward numerical integration rule, as for instance the 4-th order Runge-Kutta, would do the job perfectly well. For example, all results designated by U_4 were obtained using a programmable pocket calculator.

Figure 2. shows how the errors $U_4 - U_0$ and $U_{ex} - U_4$ behave in the region around the minimum of f. This is a good indication of the validity of numerical method. The exact result was obtained using a more advanced numerical technique[4], while U_4 was calculated by 4-th order Runge-Kutta method. The result confirmes our predictions: U_0 is a relatively good approximation of U when f is large. However, it is progressively getting worse as f becomes smaller, being well represented by the curve $U_0 - U_{ex}$. The error $U_4 - U_{ex}$, on the other hand, is practically constant regardless of the value

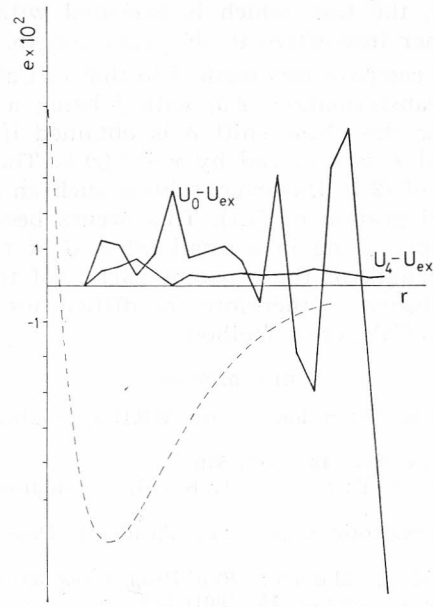

Figure 2. Stability of the errors $U_0 - U_{ex}$ and $U_4 - U_{ex}$ versus r.

of f and is smaller then $U_0 - U_{ex}$. This is in a direct agreement with our previous statement about the numerical integration of the equation for Z.

Table I gives the results of the **S**-matrix calculation of different partial waves. We compare the results of the exact, WKB and this method, for partial waves $l = 0, 1, 15, 16, 17$. The results show that the WKB approximation is very sensitive to the relative separation of the turning points while this method practically does not notice the difference.

TABLE I

l	$\mathbf{S}_{ex}$	$\mathbf{S}_{WKB}$	$\mathbf{S}_4$
0	— 0.252 — i0.968	— 0.251 — i0.968	— 0.254 — i0.967
1	0.550 + i0.835	0.549 + i0.836	0.551 + i0.835
15	— 0.906 — i0.424	— 0.833 — i0.553	— 0.906 — i0.424
16	0.797 + i0.603	0.889 + i0.458	0.797 + i0.604
17	— 0.238 + i0.971	— 0.660 + i0.752	— 0.242 + i0.970

CONCLUSION

A method was described for solving Schrödinger equation, with special attention paid to the solutions which are of short wave lenght. Although calculating phase shifts from the WKB approximation is quicker, the results of this method are at least as accurate and independent of the relative positions of the turning points of $f(r)$. However, the disadvantage is that (2.11) has to

be solved numerically, the task which is executed with relative ease since the step length is rather insensitive to the wave length.

It is interesting to compare this method to that of Calogero[6]. In paragraph 2. we have defined transformation (2.3) with f being a function of r. Now, Calogero's equation for the phase shift δ is obtained if f is taken constant and equal to $-k^2$ and Z is replaced by $r + \delta(r)/k$. Therefore, the equation for δ is a special case of (2.4). However, solving such an equation for δ is not simpler then direct integration of (1.1). This occurs because δ is a stepwise function i. e. it is steeply rising in a small interval of r, and then becoming almost constant. The length of the constant part is of the order of the local wave length of the solution ψ, therefore the difficulties inherent in (1.1) are not resolved by using Calogero's method.

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SAŽETAK

Numerička metoda za računanje faznog pomaka

S. Bosanac

Opisan je postupak rješavanja Schrödinger-ove jednadžbe sa specijalnom namjenom za numerički brzo i stabilno računanje faznih pomaka. Schrödinger-ova se jednadžba transformira u nelinearni oblik, te se pokazuje da rješenje takove jednadžbe ne oscilira. Metoda je dakle pogodna za potrebe računanja udarnih presjeka u atomskim sudarima. U diskusiji je opisana pogodnost te metode u odnosu na neke dosada vrlo često upotrebljavane, npr. WKB-metode. Kao glavni zaključak može se navesti da se fazni pomaci računaju po manje složenom postupku tako da je upotreba složenih računskih metoda svedena na najmanju moguću mjeru.

GRUPA ZA TEORIJSKU KEMIJU
INSTITUT »RUĐER BOŠKOVIĆ«
41001 ZAGREB

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