QUANTUM MECHANICAL REACTIVE SCATTERING VIA EXCHANGE KERNELS: COMPARISON OF GRID VERSUS BASIS SET EXPANSION OF THE EXCHANGE INTERACTION

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Received 11 July 1986

In the approach to quantum mechanical reactive scattering that we have been pursuing in an earlier paper, the reactive coupling has been described by a non-local exchange interaction in a coupled-channel Schrödinger equation. The results of systematic studies undertaken to identify the most efficient way to include the exchange interaction to infinite order, i.e. exactly, are reported. We find that the grid method used previously by Dardi et al. can be made much more efficient by using gaussian quadrature grids, but that still more efficient is an expansion of the exchange operator in a set of smooth basis functions via the "inner projection" approach of Adams and Miller. Test problems studied are the collinear H + D2, D + H2, and F + H2 reactions.

1. Introduction

This paper is a continuation of our recent efforts in developing a general methodology for carrying out rigorous quantum mechanical reactive scattering calculations. The ability to carry out such calculations routinely for reactions in 3D space remains one of the most practically important problems in theoretical chemical dynamics. The major stumbling block in this area continues to be the enormous computational undertaking involved in performing such calculations, regardless of approach. However, the recent increase in availability of large-scale supercomputers has stimulated renewed interest in the theoretical community to develop computational methods for calculating quantum reactive scattering cross sections *

The approach [4] that we have been pursuing [5–9] is based on the formulation of reactive scattering developed by one of us several years ago: it is a standard coupled-channel expansion in the internal states (channels) of the reactant molecules, the important feature being that for reactive scattering one includes channels for all arrangements (i.e. reactants and products) simultaneously. Coupling between channels of the same arrangement is described by a local interaction which gives rise to inelastic processes, while coupling between channels of different arrangements – which describes the chemical reaction – appears in this approach as an exchange (i.e. non-local) interaction. (The overall picture is closely analogous to the multiconfiguration Hartree–Fock (MC HF) methodology of electronic structure theory [10]. The exchange interactions in reactive scattering, for example, arise in the same way as electronic exchange, i.e. as matrix elements between configurations with a different arrangement of the particles.) The local interactions can be handled by relatively standard coupled-channel methods [11]; it is the non-local, exchange interaction which makes reactive scattering substantially more difficult than a comparable non-reactive, inelastic scattering problem.

* Note, for example, ref. [1]. For recent reviews of quantum reactive scattering, see ref. [2]. For some recent work in quantum reactive scattering using other approaches, see ref. [3].
When reaction probabilities are small, e.g., in the tunneling threshold region of a reaction, then it has been shown [7,8] that the exchange interaction can be treated accurately by first-order perturbation theory (which for scattering theory is the distorted wave Born approximation (DWBA)), provided one treats the non-reactive interactions to infinite order. Within this perturbative limit, therefore, the procedure is that one first carries out non-reactive coupled-channel scattering calculations separately in each arrangement, and then uses these inelastic scattering wavefunctions (the "distorted waves") to compute matrix elements of the exchange interaction to first order.

More recently Dardi et al. [9] have shown how the exchange interaction can also be included to infinite order, i.e. the complete solution to the reactive scattering problem, by discretizing it on a grid in the scattering coordinate and then formally summing the distorted wave Born series. The major additional effort here, beyond that required for the perturbative treatment, is that one must solve a large set of simultaneous linear equations (i.e. invert a matrix), the order of which is the number of coupled channels included in the non-reactive expansions times the number of grid points needed to represent the kernel of the exchange interaction.

The purpose of this paper is to report the results of systematic studies we have carried out in searching for the most efficient way to include exchange to infinite order (i.e. exactly). This includes refinement and variations of the grid method used by Dardi et al. and also the use of "smooth" basis set expansions of the exchange interaction. (Since discrete grids can be thought of as basis sets of Dirac delta functions at the grid points, it is possible to think of all these approaches as "basis set methods" simply with different choices of the basis set.) Since the computational bottleneck is the size of a matrix to be inverted, it is important to minimize the number of basis functions (or grid points) needed to represent the exchange kernel accurately. The test problems that we have used for the present studies are the collinear H + D₂, D + H₂, and F + H₂ reactions.

Section 2 first briefly summarizes the basic formulation we use, and section 3 describes the results. Summarizing the latter briefly, we find that gaussian quadrature grids are significantly more efficient than the uniform grids used previously by Dardi et al., but that the use of smooth basis sets is still more efficient. The basis set expansion of the exchange kernel uses the "inner projection" that Adams and Miller [6] found earlier to be more efficient than other ways of expanding it. This expansion leads to the Schwinger variation form [12,13 p. 857] for the scattering matrix, a method that has been used extensively in recent years for electron–atom/molecule scattering [14]. Our conclusions are summarized in section 4.

### 2. Summary of methodology

The basic formulation and methodology that we use has been summarized rather completely by Dardi et al. [9] so here we give a more abbreviated overview. The reader should see section 2 of ref. [9] for the more complete presentation. As there, the present notation applies specifically to a collinear atom–diatom reaction. The generalization to 3D requires the vibrational quantum number index \( n \) to be expanded to the composite vibration–rotational quantum number index \( (n, j, K) \).

The coupled-channel equations which describe the complete inelastic and reactive scattering process are

\[
0 = \left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_0(R) - E \right) \Psi(R) + \int_0^\infty dR' \ V_x(R, R') \Psi(R'),
\]

where the bold face quantities are matrices in the channel index \( (\gamma, n) \), where \( \gamma \) is the arrangement (i.e. \( \gamma = a \) for A + BC, \( \gamma = b \) for B + AC, \( \gamma = c \) for C + AB) and \( n \) is the vibrational quantum number of the diatom in that arrangement. \( V_0 \) is the local interaction,

\[
(V_0(R))_{\gamma n, \gamma' n'} = \delta_{\gamma \gamma'} V_{\gamma, n'}(R_{\gamma}),
\]

(2.2a)
which couples states of the same arrangement, and $V_x$ is the exchange interaction,

$$\langle V_x(R, R') \rangle_{\gamma n, \gamma' n'} = V_{\gamma n, \gamma' n'}(R, R'), \quad (2.2b)$$

which couples states of different arrangements. Ref. [9] gives the explicit expressions for these interactions. Also,

$$\langle \mathcal{E} \rangle_{\gamma n, \gamma' n'} = \delta_{\gamma\gamma'}\delta_{n'n'}(E - \epsilon_{\gamma n}), \quad (2.2c)$$

where $E$ is the total energy and $\epsilon_{\gamma n}$ the vibrational energy for state $n$ of arrangement $\gamma$. (We note that a sufficient number of closed channels, i.e. those for which $E - \epsilon_{\gamma n} < 0$, as well as the open channels must be included in the coupled-channel expansion, eq. (2.1).) The radial function $f(R)$ is also a matrix in this $(\gamma n)$-space,

$$\langle f(R) \rangle_{\gamma n, \gamma' n'} = f_{\gamma n \rightarrow \gamma' n'}(R), \quad (2.3a)$$

the asymptotic form of which defines the $K$-matrix,

$$f(R) \sim s(R) + c(R)K, \quad (2.3b)$$

where $s$ and $c$ are diagonal matrices of sines and cosines

$$s(R) = v_{\gamma n}^{-1/2}\delta_{\gamma\gamma'}\delta_{n'n'}\sin(k_{\gamma n}R),$$

$$c(R) = v_{\gamma n}^{-1/2}\delta_{\gamma\gamma'}\delta_{n'n'}\cos(k_{\gamma n}R), \quad (2.3c)$$

where

$$k_{\gamma n} = \left[\frac{2\mu_{\gamma}(E - \epsilon_{\gamma n})}{\hbar^2}\right]^{1/2}, \quad v_{\gamma n} = \hbar k_{\gamma n}/\mu_{\gamma}.$$ 

The $S$-matrix, the square moduli of whose matrix elements are the inelastic and reactive transition probabilities, is then

$$S = (1 - iK)(1 - iK)^{-1}. \quad (2.4)$$

The zeroth-order radial function matrix $f_0(R)$ is the solution of the non-reactive coupled equations (i.e. eq. (2.1) with $V_x$ set to zero),

$$0 = \left( -\frac{1}{2\mu} \frac{d^2}{dR^2} + V_0(R) - \mathcal{E} \right) f_0(R), \quad (2.5a)$$

with the similar asymptotic form

$$f_0(R) \sim s(R) + c(R)K_0, \quad (2.5b)$$

where $K_0$ is diagonal in arrangement index,

$$\langle K_0 \rangle_{\gamma n, \gamma' n'} = \delta_{\gamma\gamma'}K_{\gamma n, n'}. \quad (2.5c)$$

Also needed is the non-reactive Green function $G_0$, the non-local operator whose kernel is [4,15]

$$G_0(R, R') = (-2/\hbar)f_0(R)g_0(R') = (-2/\hbar)g_0(R)f_0^*(R'), \quad R < R', \quad (2.6a)$$

$$= (-2/\hbar)g_0(R)f_0^*(R'), \quad R > R', \quad (2.6b)$$
where \( g_0(R) \) is the irregular solution to the non-reactive coupled-channel equations, eq. (2.5a), with asymptotic form

\[
g_0(R) \sim c(R),
\]

(2.6b)

“\( t \)” denotes the transpose matrix.

Eq. (2.1) can then be converted into the distorted wave Lippman–Schwinger equation [13 pp. 822–832, 16],

\[
f = f_0 + G_0 V_x f,
\]

(2.7)

which is formally solved by iteration,

\[
f = [1 + G_0 V_x + (G_0 V_x)^2 + \ldots] f_0.
\]

(2.8)

By considering the asymptotic limit, \( R \rightarrow \infty \), of \( f(R) \) in eq. (2.8), and using eqs. (2.3), (2.5) and (2.6), one can readily identify the following distorted wave Born series for the \( K \)-matrix,

\[
K = K_0 + (-2/\hbar) \langle f_0 | (1 - V_x G_0)^{-1} V_x | f_0 \rangle,
\]

(2.9)

where the bra–ket symbols denote a matrix element over the translational coordinate \( R \). This series can be summed formally to give

\[
K = K_0 + (-2/\hbar) \langle f_0 | (1 - V_x G_0) V_x | f_0 \rangle,
\]

(2.10a)

or

\[
K - K_0 + (-2/\hbar) \langle f_0 | V_x (1 - V_x G_0)^{-1} V_x | f_0 \rangle,
\]

(2.10b)

or other equivalent forms.

The above infinite-order expression, eq. (2.10), can be made practically useful if one imagines evaluating the various integrals in eq. (2.9) by quadrature, e.g.,

\[
\langle f_0 | V_x G_0 V_x | f_0 \rangle = \int_0^\infty dR \int_0^\infty dR' \int_0^\infty dR'' \int_0^\infty dR''' f_0(R) V_x(R, R') G_0(R', R'') V_x(R'', R''') f_0(R''')
\]

\[
= \sum_{i,i',i'',i'''} w_i w_{i'} w_{i''} w_{i'''} f_0(R_i) V_x(R_i, R_{i'}) G_0(R_{i'}, R_{i''}) V_x(R_{i''}, R_{i'''}) f_0(R_{i'''}),
\]

(2.11b)

where \( \{ R_i \} \) are the quadrature points and weights. By introducing the composite index \( (i\gamma n) \), the quantity in eq. (2.11b) is recognized to be the matrix product

\[
f_i^0 V_x G_0 V_x f_0.
\]

(2.11c)

Here \( V_x \) and \( G_0 \) are the following square matrices in this composite index:

\[
(V_x)_{i\gamma n,i'\gamma' n'} = \sqrt{w_i w_{i'}} V_{\gamma n,\gamma' n'}(R_i, R_{i'}),
\]

(2.12a)

\[
(G_0)_{i\gamma n,i'\gamma' n'} = \sqrt{w_i w_{i'}} \delta_{\gamma \gamma'} G_{i, n, n'}(R_i, R_{i'}),
\]

(2.12b)

and \( f_0 \) is a rectangular matrix

\[
(f_0)_{i\gamma n,\gamma' n'} = \sqrt{w_i} \delta_{\gamma \gamma'} f_{n, n'}(R_i).
\]

(2.12c)
A similar identification is possible for all the terms in eq. (2.9), so that its sum is a matrix version of eq. (2.10) in the composite \((i\gamma n)\)-space,

\[
K = K_0 + (-2/h)\mathbf{f}_0 (1 - V_s G_0)^{-1}V_s \mathbf{f}_0.
\]  

(2.13)

Here \(\mathbf{f}_0\), \(V_s\), and \(G_0\) are the matrices in eq. (2.12).

Eq. (2.13) is the working equation for the "grid method" used by Dardi et al. [9] and also in this paper. As noted in section 1, the key feature of the calculation is the matrix inverse which involves a matrix in the composite \((i\gamma n)\) index and is thus of dimension \((\text{number of grid points } \{R_j\}) \times (\text{number of channels } \{\gamma_n\})\).

An alternative to summing the distorted wave Born series on a grid, as above, is to expand the exchange operator \(V_s\) in a basis set. Adams and Miller [6] found that the "inner projection" expansion was most efficient; here \(V_s\) is replaced as follows

\[
\mathbf{V}_s \rightarrow \sum_{k,k' = 1}^{N} V_s |u_k \rangle \langle u_k| \mathbf{V}_s |u_{k'} \rangle \langle u_{k'}| V_s.
\]  

(2.14)

where \(\{ u_k(R) \}\) is some convenient set of linearly independent functions and where the inverse matrix is in the composite space \((k\gamma n)\). (The basis \(\{ u_k \}\) need not be orthogonal or normalized.) It is clear that eq. (2.14) becomes an exact representation of \(V_s\) as the basis \(\{ u_k \}\) becomes complete. With this separable approximation to the exchange interaction the distorted wave Born series, eq. (2.9), can be summed without further approximation, giving

\[
K = K_0 + \frac{-2}{h} \sum_{k,k' = 1}^{N} \langle t_0 | \mathbf{V}_s | u_k \rangle \langle u_k| \mathbf{V}_s - \mathbf{V}_s G_0 \mathbf{V}_s | u_{k'} \rangle \langle u_{k'}| \mathbf{V}_s | t_0 \rangle.
\]  

(2.15a)

One recognizes this expression as a form of the Schwinger variational principle [12,13 p. 857]. One also recognizes eq. (2.15a) as a basis set approximation to the formally exact expression eq. (2.10b), again illustrating that it becomes exact as the basis set becomes complete. The practical question, of course, is how many basis functions are needed to obtain accurate results.

Eq. (2.15a) can be written more succinctly as

\[
K = K_0 + (-2/h) A^\dagger \mathbf{M}^{-1} A,
\]  

(2.15b)

where \(A\) is the rectangular matrix

\[
A_{k\gamma n,k'\gamma n'} = \sum_{n'} \int_0^\infty dR_\gamma \int_0^\infty dR_\gamma' u_k(R_\gamma) V_{\gamma n\gamma n'}(R_\gamma, R_\gamma') f_{n'\gamma n}(R_\gamma'),
\]  

(2.16a)

and \(\mathbf{M}\) is the square matrix

\[
M_{k\gamma n,k'\gamma n'} = \int_0^\infty dR_\gamma \int_0^\infty dR_\gamma' u_k(R_\gamma) V_{\gamma n\gamma n'}(R_\gamma, R_\gamma') u_{k'}(R_\gamma')

- \sum_{\gamma''n'',n'''} \int_0^\infty dR_\gamma \int_0^\infty dR_\gamma'' \int_0^\infty dR_\gamma''' \int_0^\infty dR_\gamma'' u_k(R_\gamma) V_{\gamma n\gamma n''}(R_\gamma, R_\gamma') u_{k'}(R_\gamma')

\times G_{n'n''n'''}(R_\gamma'', R_\gamma''') V_{\gamma''n''n'''}(R_\gamma''', R_\gamma'') u_k(R_\gamma).\]  

(2.16b)

Since the integrals in eq. (2.16) will in general have to be evaluated by numerical quadrature, which we have already noted is a matrix multiplication process, the quadrature version of eq. (2.16) can be written as

\[
A = \mathbf{U} \mathbf{V}_s t_0,
\]  

(2.17a)

\[
\mathbf{M} = \mathbf{U}(V_s - V_s G_0 V_s) \mathbf{U}^\dagger,
\]  

(2.17b)
where $U$ is the rectangular matrix

$$U_{kyn',i'yn'} = \delta_{\gamma \gamma'}\delta_{n n'}\sqrt{w_k}(R_i)$$  \hspace{1cm} (2.17c)

and $V_k$, $G_{0i}$, and $f_i$ are the matrices in "grid point space" defined by eqs. (2.12).

The important feature of eq. (2.15) is that the matrix to be inverted there is in the composite space $(k\gamma n)$, whose dimension is (number of basis functions $\{u_k\}$) $\times$ (number of channels $(\gamma n)$). If the number of basis functions $\{u_k\}$ needed for converging the inner expansion of the exchange interaction is less than the number of grid points $\{R_i\}$ needed to evaluate the numerical integrals accurately, then eq. (2.15) will win out over the grid method, eq. (2.13).

3. Results

In order to assess the utility of the various techniques described in section 2, calculations for collinear $H + D_2$ and $D + H_2$ reactions were carried out using a standard model potential [17]. In all cases a grid of approximately 1000 points was employed in the Numerov construction of the non-reactive scattering functions and Green function. Convergence studies indicate that 4--8 vibrational eigenfunctions are required in the coupled-channel expansion, eq. (2.1), for the energy ranges treated in the present report (4 for low energies, 8 for higher energies). In all cases, convergence was established by increasing the number of vibrational eigenfunctions and grid points used for the non-reactive calculation, and the number of quadrature points or basis functions employed to describe exchange, until the reaction probabilities converged and the scattering matrix ($S$-matrix) was unitary to within a few percent. Fig. 1 shows converged reaction probabilities obtained from calculations employing the techniques described in section 2. These results are in good accord with those obtained by other workers using different methods. Although reliable reaction probabilities are obtained from any of the described numerical techniques, the computationally preferable method is that which minimizes the order of the matrix to be inverted, since this is the computational bottleneck in the present approach. The computational results for these various techniques are summarized below.

![Fig. 1](image-url)  
Fig. 1. Reaction probabilities for (a) the $H + D_2(v = 0) \rightarrow HD(v = 0) + D$ and (b) the $D + H_2(v = 0) \rightarrow DH(v = 0) + H$ reaction as a function of total energy. The data plotted are obtained from: (solid curve) converged basis set "inner projection" method, ($\times$) evenly spaced grid method, (O) gaussian quadrature grid method, (squares) previous calculations [17].
3.1. Grid method

Dardi et al. [9] used the grid method, eq. (2.13), with an equally spaced grid and uniform weights \( \{ w_i \} \). This corresponds to evaluating the integrals, such as eq. (2.11), by the trapezoid rule. One knows that gaussian quadrature [18] points and weights are in general more efficient for numerical integration, so they should provide a more efficient grid for evaluating eq. (2.13).

We do indeed find this to be true. A Gauss–Hermite quadrature [18] was found to be most efficient, requiring 20–30 quadrature points to produce the results in fig. 1. A regular Tschebycheff quadrature [18] was almost as good. On the other hand, 60–100 eV evenly spaced grid points were required, and in fact for the highest energies convergence could not be achieved due to storage limitations (a CRAY 1 was used for these calculations).

3.2. Basis set (inner projection) method

Several basis sets were used for the functions \( \{ u_k(R) \} \) in eq. (2.15). Harmonic oscillator functions, i.e.

\[
\begin{align*}
  u_k(R) & \propto \exp\left[ -\frac{1}{2} b^2 (R - R_0)^2 \right] H_k [b(R - R_0)],
\end{align*}
\]

(3.1)

![Fig. 2. Reaction probabilities for (a) the F+H\(_2\)(v = 0) → FH(v = 2) + H, (b) the F+H\(_2\)(v = 0) → FH(v = 3) + H, and (c) the F+H\(_2\)(v = 1) → FH(v = 4) + H reaction as a function of total energy. The smooth curves represent converged basis set “inner projection” results while the circles show previous calculations [22].](image-url)
where $H_k$ is the $k$th Hermite polynomial [19], Tschebycheff functions [19] and floating gaussians [20],

$$u_k(R) \propto \exp\left[-\frac{1}{2}b^2(R - R_k)^2\right]. \quad (3.2)$$

spaced on a uniform \{ $R_k$ \} in the interaction region, all gave similar results. In all cases 8-16 basis functions gave the converged values in fig. 1.

Thus only half as many basis functions are required in eq. (2.15) as gaussian quadrature points in eq. (2.13) to obtain the converged reaction probabilities in fig. 1. Assuming that the matrix inversion step would be rate-determining for a large calculation, this indicates that the basis set approach would be approximately an order of magnitude ($\approx 2^3$) more efficient than the gaussian quadrature grid method.

To test the inner projection, basis set approach on perhaps a more challenging, less symmetrical example, these calculations were also carried out for the collinear $F + H_2$ reaction employing the Muckerman-5 potential surface [21]. A grid of approximately 5000 grid points was required in the Numerov calculation of the non-reactive scattering functions and Green function, the reason for this increase being due to the heavier reduced mass contained in the translational kinetic energy operator. Since three HF vibrational states are open at the threshold for reaction, more HF vibrational functions are required in the expansion eq. (2.1), in this case 8-14 HF and 6-10 $H_2$ vibrational functions provide converged results throughout the energy spectrum presented here. 8-16 harmonic oscillator functions of eq. (3.1) or floating gaussian functions were again sufficient for the expansion of the exchange interaction.

Converged reaction probabilities for the transitions $0 \rightarrow 2$, $0 \rightarrow 3$, and $1 \rightarrow 4$ [the notation $v \rightarrow v'$ refers to the reaction $F + HH(v) \rightarrow FH(v') + H$] are shown in fig. 2 and are seen to be in good accord with results obtained from other workers employing different methods [22]. The main point here is that separable expansions of the exchange potential provide reliable reaction probabilities throughout a wide region of energy. It is particularly gratifying to see that the resonance region, where coupling is the most severe, is described correctly.

Finally, fig. 3 shows a typical result for the $F + H_2$ reaction with a relatively small number of channels, 5 HF and 2 $H_2$ vibrational states. This is too few to give the completely converged results in fig. 2, but they do show that semi-quantitatively accurate results are obtained over the low-energy region even with a relatively small number of channels in the expansion.

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Fig. 3. Reaction probabilities for (a) the $F + H_2(v = 0) \rightarrow FH(v = 2) + H$ and (b) the $F + H_2(v = 0) \rightarrow FH(v = 3) + H$ reaction as a function of total energy. The smooth curves represent converged basis set "inner projection" results while the circles show results obtained from calculations using 2 $H_2$ and 5 HF vibrational channels in eq. (2.1).
4. Concluding remarks

The principal conclusion of the paper is that the inner projection expansion of the exchange interaction, eq. (2.14), and the resulting Schwinger-type basis set expansion for the $K$-matrix, eq. (2.15), is significantly more efficient than the grid expansion, even if gaussian quadrature grid points are used. I.e. one needs fewer basis functions than grid points (approximately half as many) to represent the exchange interaction sufficiently accurately.

As emphasized before [9] for the grid method, the inner projection basis set expansion also leads to expressions that require straightforward linear algebraic calculations and are thus easily vectorized for modern supercomputers. We also note a recent very interesting paper by Schneider [23] which describes a powerful new algorithm for evaluating expressions like eq. (2.15b) for very large matrices. This should be very useful for the present type of calculation.

The present methodology is ready to be applied to $A + BC$ reactions in 3D space. This requires, first, non-reactive coupled-channel calculations involving rotational and vibrational states. The dimension of the matrix $M$ of eq. (2.15b) is thus the number of rotational–vibrational states (in all arrangements) times the number of basis functions needed to expand the exchange interactions. The number of rotational–vibrational states for the $F + H_2$ reaction, for example, could be as many as a few hundred, so that the dimension of $M$ could be a few thousand. This, however, should not be an unreasonable calculation for modern supercomputers. We also note that any approximation to the non-reactive coupled-channel equations, e.g., the “coupled states” helicity conserving approximation (for a review, see ref. [24]) can readily be incorporated into the present approach, as was done in the earlier [8] perturbative treatment of exchange.

Acknowledgement

MRH is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract No. DE-AC03-76SF00098. The calculations reported herein were carried out on IBM 4381 and CRAY 1 computers supported through the National Science Foundation, Grant No. CHE84-16345.

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