Fermi resonance-algebraic model
for molecular vibrational spectra *

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Abstract

A Fermi resonance-algebraic model is proposed for molecular vibrations, where a U(2) algebra is used for describing the vibrations of each bond, and Fermi resonances between stretching and bending modes are taken into account. The model for a bent molecule XY₂ and a molecule XY₃ is successfully applied to fit the recently observed vibrational spectrum of the water molecule and arsine (AsH₃), respectively, and results are compared with those of other models. Calculations show that algebraic approaches can be used as an effective method for describing molecular vibrations with small standard deviations.

Keywords  U(2) algebra  Vibrational spectra  Fermi resonance

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Algebraic methods have been applied to molecular systems for a number of years, and a recent review \cite{ref1} is available. U(4) and U(2) algebraic model have mostly been used so far for a description of rovibrational spectra of molecules. U(4) model has two advantages that rotations and vibrations are treated simultaneously, and that Fermi resonances are described by the nondiagonal matrix elements of Majorana operators. But it becomes quite complicated when the number of atoms in a molecule is larger than 4. U(2) model is particularly well suited for dealing with the stretching vibrations of polyatomic molecules, and currently under further development \cite{ref2\sim\ref{ref5}}.

Recently, an important development on these methods is to incorporate bending vibrational modes of polyatomic molecules. Sample molecules such as acetylene \cite{ref6}, as well as $X_3$ \cite{ref2} and $XY_4$ \cite{ref5,ref7} molecules have been studied via algebraic methods. These approaches suffer from the neglect of the Fermi resonance interactions between stretching and bending modes. Due to their importance as a mechanism for intramolecular energy transfer and for descriptions of excited stretching and bending vibrations, Fermi resonances have been taken into account in simple Fermi resonance-local mode models for bent triatomic \cite{ref8} and pyramidal $XH_3$ \cite{ref9} systems and in boson-realization models for bent triatomic \cite{ref10} and $XY_4$ \cite{ref11} molecules. In this paper we will introduce a Fermi resonance-algebraic model, where a U(2) algebra is used for describing the vibration of each bond. Our method is addressed for a bent molecule $XY_2$ and a molecule $XY_3$, where Fermi resonances between the stretch and the bend are considered. In a limit, the model corresponds to the boson-realization model. Vibrational spectra of two sample molecules $H_2O$ and $AsH_3$ are used to test our model. This method can be extended for describing the vibrations of molecules with other symmetry. The corresponding results will be discussed elsewhere.

1. Hamiltonian

Let $n$ be the total degrees of freedom of vibrations and $m$ the degrees of freedom of stretching vibrations in a polyatomic molecule. We introduce $n$ U(2) algebras to describe vibrations: $U_i(2)$ ($1 \leq i \leq m$) for stretching modes and $U_\mu(2)$ ($1 + m \leq \mu \leq n$) for bending modes. Each $U_\alpha(2)$ ($1 \leq \alpha \leq n$) is generated by the operators
\{\hat{N}_\alpha, \hat{J}_{+,\alpha}, \hat{J}_{-,\alpha}, \hat{J}_{0,\alpha}\}, \text{satisfying the following commutation relations:}

\begin{align}
\{\hat{J}_{0,\alpha}, \hat{J}_{\pm,\beta}\} &= \pm \delta_{\alpha\beta} \hat{J}_{\pm,\alpha}, \quad \{\hat{J}_{+,\alpha}, \hat{J}_{-,\alpha}\} = 2\delta_{\alpha\beta} \hat{J}_{0,\alpha}, \\
[\hat{N}_\alpha, \hat{J}_{0,\beta}] &= 0, \quad [\hat{N}_\alpha, \hat{J}_{\pm,\beta}] = 0.
\end{align}

(1.1)

where \(\hat{N}_\alpha\) is related with the Casimir operator of U(2):

\[2\hat{J}_{0,\alpha}^2 + \hat{J}_{+,\alpha} + \hat{J}_{-,\alpha} = \hat{N}_\alpha(\hat{N}_\alpha/2 + 1).\]

The local basis states for each bond are written as \(|N_\alpha, v_\alpha\rangle\), where \(N_\alpha\) is the eigenvalue of \(\hat{N}_\alpha\) and \(v_\alpha\) the number of quanta on the \(\alpha\)th bond. The action of \(\hat{J}_{\pm,\alpha}\) on the local states is given by

\[\hat{J}_{+,\alpha} |N_\alpha, v_\alpha\rangle = \sqrt{v_\alpha(N_\alpha - v_\alpha + 1)} |N_\alpha, v_\alpha - 1\rangle,\]
\[\hat{J}_{-,\alpha} |N_\alpha, v_\alpha\rangle = \sqrt{(v_\alpha + 1)(N_\alpha - v_\alpha)} |N_\alpha, v_\alpha + 1\rangle.\]

(1.2)

Those \(N_\alpha\) of equivalent bonds are equal to each other: \(N_i = N_s\), and \(N_b = N_b\), where footnotes \(s\) and \(b\) refer to the stretching and the bending vibrations, respectively.

Due to Fermi resonances in the considered system, we will take \(V = V_s + V_b/2\) as a conservative quantity, where \(V_s\) and \(V_b\) is the total number of phonons of stretching and bending modes, respectively. Define the scale transformations for convenience:

\[a_\alpha \equiv \hat{J}_{+,\alpha} / \sqrt{N_\alpha}, \quad a^\dagger_\alpha \equiv \hat{J}_{-,\alpha} / \sqrt{N_\alpha}.\]

(1.3)

In the limit of \(N_s \to \infty\) and \(N_b \to \infty\), \(a_\alpha(a^\dagger_\alpha)\) reduce to bosonic operators with usual boson commutation relations [2].

In the following, we will present the vibrational model in terms of Eq. (1.3) for two molecular systems with different symmetries.

1.1 The model for vibrations of a bent molecule XY₂

For a bent triatomic molecule, we have \(n = 3\) and \(m = 2\). The Hamiltonian, where the interactions are taken up to the fifth orders, is given as follows:
\[ H = \sum_{i=1}^{2} a_i^\dagger a_i (\omega_s + x_s a_i a_i^\dagger) + a_3^\dagger a_3 (\omega_b + x_b a_3 a_3^\dagger) + \lambda_1 (a_1^\dagger a_2 + a_2^\dagger a_1) \\
+ \lambda_2 (a_1^\dagger a_1 a_2^\dagger a_2) + \lambda_3 (a_1^\dagger a_1 a_2 a_2 + H.c.) + \lambda_4 (a_1^\dagger a_2 + a_2^\dagger a_1) (a_1^\dagger a_1 + a_2^\dagger a_2) \\
+ \lambda_5 (a_1^\dagger a_2 + a_2^\dagger a_1) a_3 a_3 + \lambda_6 (a_1^\dagger a_1 + a_2^\dagger a_2) a_3^\dagger a_3 + \lambda_7 \{ (a_1^\dagger + a_2^\dagger) a_3 a_3 + H.c. \} \\
+ \lambda_8 \{ a_1^\dagger a_2^\dagger (a_1 + a_2) a_3 a_3 + H.c. \} + \lambda_9 \{ (a_1^\dagger a_1 a_1 + a_2^\dagger a_2 a_2) a_3 a_3 + H.c. \} \\
+ \lambda_{10} \{ (a_1^\dagger a_1 a_2 + a_2^\dagger a_2 a_1) a_3 a_3 + H.c. \} + \lambda_{11} \{ (a_1^\dagger + a_2^\dagger) a_3^\dagger a_3 + H.c. \}, \]

(1.4)

where \( \omega \) and \( x \) are used for comparison with the constants in the Morse potential.

\( \lambda_i \) (1 \( \leq i \leq 11 \)) are the coupling constants. The term with \( \lambda_7 \) describes the Fermi resonance between the stretching and the bending vibrations. The last four terms in Eq. (1.4) are the fifth order interactions caused by Fermi resonance. In the limit of \( N_s \rightarrow \infty \) and \( N_b \rightarrow \infty \), Eq. (1.4) corresponds to the boson-realization model \(^{10} \).

### 1.2 The model for vibrations of a molecule XY₃

For a \( C_{3v} \) symmetric molecule, we have \( n = 6 \) and \( m = 3 \). From the standard method of group theory, it is not difficult to obtain the character table, the representation matrices of the generator, and the Clebsch-Gordan coefficients of the \( C_{3v} \) group. From that knowledge, Hamiltonian where the interactions are taken up to the fourth orders are expressed in terms of operators Eq. (1.3):

\[ H = \sum_{i=1}^{3} a_i^\dagger a_i (\omega_s + x_s a_i a_i^\dagger) + \sum_{\mu=1}^{6} a_\mu^\dagger a_\mu (\omega_b + x_b a_\mu a_\mu^\dagger) + \eta_1 \sum_{i \neq j} a_i^\dagger a_j \\
+ \eta_2 \sum_{\mu \neq \nu} a_\mu^\dagger a_\nu + \eta_3 (a_1^\dagger a_1 a_4 + a_2^\dagger a_2 a_5 + a_3^\dagger a_3 a_6 + H.c.) \\
+ \eta_4 \{ a_1^\dagger (a_5 a_5 + a_6 a_6) + a_2^\dagger (a_4 a_4 + a_5 a_6) + a_3^\dagger (a_4 a_4 + a_5 a_5) + H.c. \} \\
+ \eta_5 \{ a_1^\dagger a_4 a_5 + a_6 + a_2^\dagger a_5 a_4 + a_6 + a_3^\dagger a_6 a_4 + a_5 + H.c. \} \\
+ \eta_6 (a_1^\dagger a_5 a_6 + a_2^\dagger a_4 a_6 + a_3^\dagger a_4 a_5 + H.c.) + \eta_7 \sum_{i \neq j} a_i^\dagger a_i a_j \\
+ \eta_8 \sum_{i \neq j} (a_1^\dagger a_i + a_i^\dagger a_j) (a_j a_j + a_j a_j) + \eta_9 \sum_{i \neq j \neq k} a_i^\dagger a_i (a_j^\dagger a_k + a_k^\dagger a_j) \\
+ \eta_{10} \sum_{i \neq j} (a_i^\dagger a_j a_j + H.c.) + \eta_{11} \sum_{i \neq j \neq k} (a_i^\dagger a_j a_k + H.c.) \]

(1.5)

where \( \omega \) and \( x \) are again used for comparison with the constants in the Morse potential.
\( \eta_1 \) and \( \eta_2 \) is the harmonic constant for the stretch and the bend, respectively. These \( \eta_p \)
\((3 \leq p \leq 6)\) are the Fermi resonance coupling constants, \( \eta_q \) \((7 \leq q \leq 11)\) anharmonic
constants of the stretching vibrations, and \( \eta_r \) \((12 \leq r \leq 15)\) anharmonic constants of
interactions between the stretch and the bend. In Eq. (1.5), we have omitted the
interaction terms for the bending vibrations, which are similar to the terms with \( \eta_q \)
\((7 \leq q \leq 11)\) for the stretching modes, and also omitted the fourth-order interactions
between the stretching and the bending vibrations. In the limit of \( N_s \rightarrow \infty \) and \( N_b \)
\rightarrow \infty, equation (1.5) reduces to the extended local mode model for three equivalent
stretching bonds \([12]\), where the bending vibrations were neglected.

2. Applications

2.1 Application to H\(_2\)O

Studies of the vibrations of the water molecule already exist in the literature. Its
stretching vibrational energy levels were calculated via nonlinear quantum theory \([13]\).
Halonen and Carrington proposed a simple vibrational curvilinear internal coordinate
hamiltonian \([8]\) for its vibrational levels up to 18,500 cm\(^{-1}\). The same levels were
studied by U(4) algebraic model \([1]\). Its recently observed vibrational spectrum up to
22,000 cm\(^{-1}\) were analyzed by the potential-energy surface from \textit{ab initio} calculation
\([14]\) as well as in the boson-realization model and the corresponding \(q\)-deformed model
\([10]\). Owing to much research on this molecule, it provides a good testing ground for
different models.

Now, we calculate the Hamiltonian matrix elements in the symmetrized bases, then
determine the 15 parameters in Eq. (1.4) by a least-squares optimization in fitting
the experimental data \(E_{\text{obs}}\) in cm\(^{-1}\) (their normal labels \((\nu_1\nu_2\nu_3)\)), taken from the
compilation of Ref. \([14]\). Two boson numbers \(N_s\) and \(N_b\) are taken to be 48 and 65,
respectively. The parameters obtained are given in cm\(^{-1}\) as follows:

\[
\begin{align*}
\omega_s = 3705.121, & \quad x_s = -4.602, & \quad \omega_b = 1599.485, & \quad x_b = 3.913, & \quad \lambda_1 = -51.335, \\
\lambda_2 = -12.746, & \quad \lambda_3 = -1.004, & \quad \lambda_4 = 3.199, & \quad \lambda_5 = -2.853, & \quad \lambda_6 = -21.956, \\
\lambda_7 = 12.686, & \quad \lambda_8 = -0.422, & \quad \lambda_9 = -5.901, & \quad \lambda_{10} = 2.187, & \quad \lambda_{11} = 4.220.
\end{align*}
\]
The observed and calculated vibrational levels are presented in Table 1 where our results are also compared with those calculated in the boson-realization model \cite{10}. The $\Delta E_{cal}$ are the differences between the observed and the calculated values. The standard deviation (SD) of this fit is 6.724 cm$^{-1}$, while that of the boson-realization model and the corresponding $q$-deformed model is 8.198 cm$^{-1}$ and 7.157 cm$^{-1}$ \cite{10}, respectively. The present model applied to H$_2$O gives a slight improvement in the fit to its vibrational energy levels.

### 2.2 Application to AsH$_3$

To our knowledge, vibrations of a molecule XY$_3$ have not been studied via algebraic methods yet. As an example, we now apply Eq. (1.5) to the vibrational spectrum of arsine (AsH$_3$). The calculation of energy levels will be greatly simplified if the symmetrized bases are used. For the considered system, these bases can be obtained by the method of Ref. \cite{7}. This method is particularly useful when describing vibrations of polyatomic molecules and for high overtones.

Recently observed data ($E_{obs}$) of AsH$_3$ with their normal labels ($\nu_1\nu_2\nu_3\nu_4\nu_5\nu_6$) are taken from the compilation of Refs. \cite{9,15}. Since there are 18 experimental data for this molecule it is not possible to determine all coupling constants in Eq. (1.5) by a least-squares optimization. It is natural to choose the following parameters in Eq. (1.5) nonvanishing: $\omega_s$, $x_s$, $\omega_b$, $x_b$, $\eta_1$, $\eta_2$, $\eta_3$, $\eta_4$, $\eta_5$, and $\eta_6$. In other words, we neglect the terms with $\eta_t$ ($7 \leq t \leq 11$). We have found out that other choice does not provide improvement in our fits. For comparison, we have made the first fit (Fit a) where the model is in the limit of $N_s \to \infty$ and $N_b \to \infty$. The obtained parameters and the calculated differences ($\Delta E_{cal}^a$) with the corresponding observed data ($E_{obs}$) in this fit are listed in Table 2 and 3. In another fit (Fit b) we take the boson numbers $N_s$ and $N_b$ to be 62 and 42, respectively. The results in Fit b are also listed in the related Tables.
The SD in Fit a and b is 10.201 cm\(^{-1}\) and 5.827 cm\(^{-1}\), respectively. The calculated results for this molecule in Fit b can be compared with those by Lukka et al\(^{[9]}\). However, their vibrational Hamiltonian was expressed in terms of curvilinear internal coordinates, and the Morse oscillator basis functions and the results of \textit{ab initio} calculation were used there.

3. Conclusion and discussion

We have proposed Fermi resonance-algebraic models for the vibrations of a bent molecule XY\(_2\) and a molecule XY\(_3\) by U(2) algebras for the description of both stretching and bending modes, where Fermi resonances between the stretch and the bend are considered. In the limit, the models reduce to the recently presented boson-realization models. As an example, they have been applied to vibrational spectra of the water molecule and arsine (AsH\(_3\)). To some extent, they have provided improvement in the standard deviations in the corresponding boson-realization models for the same observed energy levels. It needs more sample calculations to judge which approach is better.

The present calculations and others \(^{[2\sim7,10,11]}\) demonstrate that an algebraic approach can be used as an effective method for describing molecular vibrations with good precision. In this approach the eigenvalues and the related wave functions are obtained through matrix diagonalization. Hence, the required computing time is short, and some other physical properties, such as transition intensities \(^{[5,11]}\), are allowed to calculate. It provides the possibility of using an algebraic model as a numerically efficient, phenomenological theory for studying molecular spectra, especially when no \textit{ab initio} calculation is available.

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TABLE 1. Observed and calculated vibrational energy levels of $H_2O$ (cm$^{-1}$)

| $(\nu_1\nu_2\nu_3)$ | $E_{\text{obs}}^{[14]}$ | $\Delta E_{\text{cal}}^{[10]}$ | $\Delta E_{\text{cal}}^{[10]}$ | $(\nu_1\nu_2\nu_3)$ | $E_{\text{obs}}^{[14]}$ | $\Delta E_{\text{cal}}^{[10]}$ | $\Delta E_{\text{cal}}^{[10]}$ |
|----------------------|--------------------------|-----------------------------|-----------------------------|----------------------|--------------------------|-----------------------------|-----------------------------|
| (010)                | 1594.7498                | -2.668                      | -4.733                      | (001)                | 3755.93                  | 0.170                       | -0.522                      |
| (020)                | 3151.63                  | 0.016                       | -4.136                      | (011)                | 5331.269                 | -5.434                      | -5.562                      |
| (100)                | 3657.053                 | 3.549                       | 1.997                       | (021)                | 6871.51                  | -3.398                      | -4.325                      |
| (030)                | 4666.793                 | 5.464                       | 0.110                       | (010)                | 7249.81                  | 2.611                       | 0.409                       |
| (110)                | 5234.977                 | 1.684                       | 0.694                       | (031)                | 8373.853                 | 4.051                       | 2.443                       |
| (040)                | 6134.03                  | 9.088                       | 4.828                       | 8807                 | -1.858                   | -0.673                      |
| (120)                | 6775.1                   | 1.817                       | -0.591                      | (041)                | 9833.584                 | 13.643                      | 12.564                      |
| (200)                | 7201.54                  | 1.302                       | 0.483                       | (121)                | 10328.731                | -0.616                      | -0.006                      |
| (002)                | 7445.07                  | 3.063                       | 1.453                       | (201)                | 10613.355                | 0.766                       | -0.809                      |
| (050)                | 7552                     | 11.254                      | 10.415                      | (211)                | 11032.406                | 5.575                       | 3.577                       |
| (130)                | 8273.976                 | 0.594                       | -1.912                      | (013)                | 11813.19                 | 2.636                       | 1.919                       |
| (210)                | 8761.582                 | 0.248                       | 1.828                       | (211)                | 12151.26                 | -3.666                      | 0.371                       |
| (060)                | 8890                     | -17.089                     | -12.506                     | (013)                | 12565                    | -9.461                      | -6.151                      |
| (012)                | 9000.136                 | -5.600                      | -4.650                      | (141)                | 13256                    | 4.292                       | 4.464                       |
| (220)                | 10284.367                | -0.405                      | -0.714                      | (221)                | 13652.656                | -3.450                      | -0.116                      |
| (022)                | 10524.3                  | -0.950                      | -0.991                      | (301)                | 13830.938                | 0.384                       | -1.448                      |
| (300)                | 10599.686                | -3.117                      | -3.002                      | (023)                | 14066.194                | -9.806                      | -7.824                      |
| (102)                | 10868.876                | 5.583                       | 1.810                       | (103)                | 14318.813                | 6.331                       | 1.985                       |
| (310)                | 12139.2                  | -6.313                      | -1.508                      | (151)                | 14640                    | -10.977                     | -5.968                      |
| (112)                | 12407.64                 | 3.124                       | 3.469                       | (231)                | 15119.029                | -3.536                      | -2.852                      |
| (042)                | 13448                    | 7.777                       | 4.483                       | (311)                | 15347.956                | -4.276                      | 1.217                       |
| (320)                | 13642.202                | -7.521                      | -4.024                      | (113)                | 15832.765                | -7.239                      | -1.381                      |
| (202)                | 13828.277                | 2.052                       | 0.344                       | (321)                | 16821.635                | -2.039                      | 2.715                       |
| (122)                | 13910.896                | 6.188                       | -0.130                      | (203)                | 16898.842                | 3.234                       | -1.570                      |
| (400)                | 14221.161                | -1.522                      | -1.806                      | (123)                | 17312.539                | 1.834                       | -1.041                      |
| (004)                | 14536.87                 | 9.844                       | 6.393                       | (401)                | 17495.528                | 0.756                       | -0.563                      |
| (330)                | 15107                    | -14.579                     | -12.251                     | (331)                | 18265.82                 | -3.654                      | -2.516                      |
| (212)                | 15344.503                | 12.518                      | 10.038                      | (213)                | 18393.314                | -1.400                      | 0.480                       |
| (410)                | 15742.795                | 0.179                       | 4.839                       | (411)                | 18989.961                | -12.986                     | -0.621                      |
| (222)                | 16825.23                 | -16.629                     | -18.041                     | (421)                | 19720                    | -0.801                      | -0.492                      |
| (302)                | 16898.4                  | 1.469                       | -3.711                      | (303)                | 19781.105                | 14.596                      | 8.509                       |
| (420)                | 17227.7                  | 11.514                      | 0.715                       | (501)                | 20543.137                | -7.555                      | -2.973                      |
| (500)                | 17458.354                | 0.824                       | 0.139                       | (313)                | 21221.828                | -6.455                      | -5.430                      |
| (104)                | 17748.073                | -0.279                      | -0.504                      | (232)                | 18320                    | 25.584                      | 29.589                      |
| (312)                | 18392.974                | -1.070                      | 0.979                       | (412)                | 21221.569                | -5.258                      | -5.451                      |

SD 8.198 6.724
TABLE 2. Parameters (cm\(^{-1}\)) for AsH\(_3\) obtained by the least square fitting

|     | \(\omega_s\) | \(x_s\) | \(\omega_b\) | \(x_b\) | \(\eta_1\) |
|-----|---------------|---------|--------------|---------|-----------|
| Fit a | 2039.921      | −80.580 | 959.021      | 64.320  | −24.775   |
| Fit b | 2066.972      | −28.376 | 962.647      | 68.865  | −18.639   |

|     | \(\eta_2\) | \(\eta_3\) | \(\eta_4\) | \(\eta_5\) | \(\eta_6\) |
|-----|---------|---------|---------|---------|---------|
| Fit a | −21.932 | −53.616 | −5.996  | −33.712 | 1.823   |
| Fit b | −27.283 | −55.482 | −5.850  | −29.862 | 11.970 |

TABLE 3. Observed and calculated vibrational energy levels of AsH\(_3\) (cm\(^{-1}\))

| \((\nu_1\nu_2\nu_3^l\nu_4^l)\) | \(E_{obs}^{[9,15]}\) | \(\Delta E_{cal}^a\) | \(\Delta E_{cal}^b\) | \((\nu_1\nu_2\nu_3^l\nu_4^l)\) | \(E_{obs}^{[9,15]}\) | \(\Delta E_{cal}^a\) | \(\Delta E_{cal}^b\) |
|-------------------------------|-------------------|-------------------|-------------------|-------------------------------|-------------------|-------------------|-------------------|
| \((010^00^0)\) | 906.752 | −8.425 | −1.328 | \((000^11^1)\) | 999.225 | 8.253 | 9.295 |
| \((020^00^0)\) | 1806.149 | 3.950 | 1.853 | \((010^11^1)\) | 1904.115 | −9.368 | −0.427 |
| \((000^20^0)\) | 1990.998 | −2.224 | 1.602 | \((000^02^1)\) | 2003.483 | −10.736 | −9.707 |
| \((100^00^0)\) | 2115.164 | −0.720 | 0.932 | \((001^10^0)\) | 2126.423 | 2.698 | −1.537 |
| \((110^00^0)\) | 3013 | 1.704 | 3.953 | \((011^11^1)\) | 3102 | −0.615 | 3.396 |
| \((200^00^0)\) | 4166.772 | −0.182 | 3.033 | \((101^10^0)\) | 4167.935 | −8.389 | −2.245 |
| \((300^00^0)\) | 6136.316 | 2.401 | −4.667 | \((201^10^0)\) | 6136.310 | 9.419 | 1.951 |
| \((003^00^0)\) | 6276 | −3.991 | −2.321 | \((102^20^0)\) | 6295 | 2.410 | 2.238 |
| \((400^00^0)\) | 8028.977 | −2.275 | −1.389 | \((301^10^0)\) | 8028.969 | 1.398 | 0.713 |

| SD | 10.201 | 5.827 |