Analysis of vibrational dependence of the isotropic part of the intermolecular potential

A.D. Bykov, V.M. Mikhailov, and V.N. Stroinova

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

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General equations have been derived for studying the effect of the degree of vibrational excitation of an absorbing molecule on the isotropic part of the intermolecular interaction potential. The intermolecular potential for the collision of two He atoms is analyzed numerically. The effective operator of the intermolecular potential is constructed with the help of coupled cluster theory of rotational-vibrational interactions. The asymptotic series of the perturbation theory for the effective operator of the intermolecular potential in the first Pade approximant is evaluated.

Introduction

Studying the vibrational dependence of the potential on the intermolecular interaction is an urgent problem in molecular spectroscopy. The dependence of the intermolecular potential (IMP) on the degree of vibrational excitation of an absorbing molecule is most pronounced for lines formed by transitions to highly excited vibrational states, when intramolecular effects, such as anharmonism of vibrations, Fermi and Darling–Dennison accidental resonances become dominating.

The relaxation parameters of spectral lines: halfwidth, line shift, cross-relaxation parameters, determine the shape of the line profile, and they should be calculated to rather high accuracy for correct assignment of high-resolution experimental data.

To calculate the relaxation parameters, one should first determine IMP constants and their vibrational dependence. These data are, as a rule, unavailable in the literature, and therefore reconstruction of IMP characteristics, in particular, for highly excited vibrational states from measured line shifts[1–3] by solving the inverse problem or calculation of the vibrational dependence of IMP[4] are rather urgent problems. It should be noted that some *ab initio* calculations of the intermolecular interaction potential are available,[5] but only for the ground state neglecting its dependence on the degree of vibrational excitation.

In the theory of spectral line broadening, it is accepted to consider the IMP of two colliding molecules as a sum of two terms: isotropic and anisotropic (depending on orientation of molecules) parts: $V(R) = V_{iso}(R) + V_{aniso}(R, \theta)$, where R is the separation between the centers of gravity of the colliding molecules; θ is a set of angles describing their mutual orientation. The aim of this paper is to derive general equations for studying the dependence of the isotropic part of the IMP on the degree of vibrational excitation of a molecule. We consider the vibrational dependence of the isotropic part of the intermolecular potential, since it is just this part of the IMP that determines the coefficients of line shift by buffer-gas pressure.[1–3] The asymptotic expansion of $V_{iso}(R)$ in an inverse power series in R is grouped in such a way that the first terms of the new series have a correct asymptotic dependence on the intermolecular separation. The re-grouped series is then summed with the use of Pade approximants. To determine the vibrational dependence, we use the theory of limiting linked schemes[6] for ordering rotational-vibrational interactions. In the limiting scheme corresponding to the model of the so-called overexcited oscillator,[6] the effective operator of the potential $V_{iso}(R)$ is presented as a power series over vibrational variables for an elementary rotational excitation. To sum up the asymptotic series of the perturbation theory for the effective operator of the potential $V_{iso}(R)$, we also apply the method of Pade approximants. The potential $V_{iso}(R)$ for different systems of colliding molecules is analyzed in the approximation of the first Pade approximant for different overtones and combination tones.

The results of this work can be used in data banks and atlases of spectroscopic information; they are also useful in solving problems of the laser beam propagation through the atmosphere. Besides, the obtained results may prove to be useful in calculation of the time of V–V-exchange and V–T-relaxation.

Dependence of line shift on the isotropic part of intermolecular potential

As was shown earlier[1–3] the shift of lines due to transitions to highly excited vibrational states is

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determined mostly by the change of the isotropic part of the potential $V_{iso}(R)$ at vibrational excitation of the absorbing molecule. Within the framework of the Anderson—Tsao—Curnutte method, the relaxation parameters (line shift and halfwidth) are described by the following equation[7]:

$$\gamma_{if} - i\delta_{if} = \frac{n}{c} \sum_j \rho(j) \int_0^\infty F(v)\, v\, dv \times$$

$$\times \left(\frac{b_c^2}{2} + \int_{b_c}^\infty db\, b\, S_{if}(j, b, v) \right); \quad (1)$$

$$S_{if}(j, b, v) = S_1 + S_2, \quad (2)$$

$$S_1 = \frac{1}{\hbar} \int_{-\infty}^{+\infty} dt\, [\langle v_f | V_{iso}(R) | v_f \rangle - \langle v_i | V_{iso}(R) | v_i \rangle]. \quad (3)$$

Here i and f are quantum numbers of the initial and final vibrational states; γ_{if} is the line halfwidth; δ_{if} is the line shift; $\rho(j)$ is the density matrix of the disturbing molecule; $F(v)$ is the Maxwell distribution function; b_c is the Anderson truncation parameter; $S_{if}(j, b, v)$ is the truncation function written as a sum of terms of the first and second orders of the perturbation theory. The real part of S_2 contributes to the line halfwidth, whereas the imaginary part of S_2 and S_1 determines the line shift. In Eq. (3) the function S_1 depends on the difference of the matrix elements of the operator $V_{iso}(R)$, where $|v_i\rangle$ are the vibrational wave functions of the initial state, and $|v_f\rangle$ are those of the final state. The potential $V_{iso}(R)$ can be represented as a sum of contributions coming from the inductive and dispersion energy of interaction of colliding particles: $V_{iso}(R) = V_{ind}(R) + V_{disp}(R)$. Using the London approximation,[8,9] we can write the isotropic part of the IMP as an inverse power series in R:

$$V_{iso}(R) = \sum_{n=6}^\infty \frac{C_n}{R^n}. \quad (4)$$

In Eq. (4) C_n are the constants depending on some integrals including electronic wave functions. In the general case, C_n depend on the instantaneous configuration of nuclei and are functions of vibrational coordinates. The series (4) is an example of application of the perturbation theory, in the Rayleigh—Schrödinger formalism, for the case of remote interaction. In practical calculations, the vibrational dependence of the coefficients C_n is usually neglected and consideration is restricted to the first term of the series (4) that is proportional to $1/R^6$. As known, the first term of Eq. (4) corresponds to the sum of the inductive interaction of the dipole–induced-dipole type and the dispersion interaction corresponding to the dipole–dipole potential. In calculation of the dispersion part of the potential, the Unsold[8,9] approximation is often used. In this approximation, the constants of the dispersion potential are expressed through polarizability and the first ionization potential of molecules. Then, integrating Eq. (3) and turning from the separation R to the impact parameter b, we can obtain:

$$S_1 = -\frac{3\pi}{8\hbar v b^5} \times$$

$$\times \left\{ (\mu_i^2 - \mu_f^2)\, \alpha_2 + \mu_2^2\, (\alpha_i - \alpha_f) + \frac{3}{2}\, \bar{\varepsilon}\, \alpha_2\, (\alpha_i - \alpha_f) \right\}. \quad (5)$$

In Eq. (5), α_2 and μ_2 are the mean polarizability and the mean dipole moment of the disturbing molecule; α_i and α_f are the quantum-mechanically mean values of the polarizability in the initial and final vibrational states of the absorbing molecule, respectively; μ_i and μ_f are quantum-mechanically mean dipole moments in the initial and final states, respectively; ε_1 and ε_2 are the ionization potentials. The function S_1 in Eq. (5) includes the contributions of only the inductive (the first and second terms in braces) and the dispersion interaction (the third term in braces).

The calculations made in Refs. 1–3 showed that the contribution of the function S_1 to the shift of lines of H_2O, SO_2, CO_2, and NO_2 molecules at broadening by N_2, O_2, and inert gas atoms dominates for lines due to transitions to highly excited vibrational states. For example, the contribution of the function S_1 in the form (5) to the shift of H_2O absorption lines at broadening by inert gases makes up from 75 to 85% of the total shift for lines due to transitions from the ground state to the vibrational state (301). In Refs. 1–3, the polarizability α_f of the excited states was determined through fitting the measured shifts of some lines, for other lines the shift was calculated by Eq. (5).

In Ref. 10, to calculate shifts of H_2O lines formed by transitions from the ground vibrational state to the states (301) and (221), the approximation (5) was also applied, but with the use of the *ab initio* polarizability of the water molecule. The calculated results from Refs. 1–3 and 10 well agree with the experiment. Reference 2 presents the vibrational dependence of the parameter α_f for the H_2O molecule; this dependence was obtained from analysis of the measured line shifts. In Ref. 11, the vibrational dependence of α_f of the H_2O molecule was analyzed numerically using Pade approximants.

Thus, the pressure shifting of lines can be a source of data on the vibrational dependence of the isotropic part of the intermolecular potential or (within the framework of the Unsold approximation) serve for estimation of polarizability of molecules in different vibrational states.

In the general case, the isotropic part of the IMP $V_{iso}(R)$ can be presented as an asymptotic series with the coefficients C_n depending on the normal coordinates q:

$$V_{\text{iso}}(R) = \sum_{n=6}^{\infty} \frac{C_n(q)}{R^n} . \quad (6)$$

It is significant that the series (6) is alternate. Earlier in Ref. 4 it was shown that the expansion of the IMP represented as a sum of Lennard–Jones potentials for every pair of atoms in a power series in terms of $1/R$ has sign-alternate coefficients.

Since the series (6) is asymptotic, a proper summation method should be applied to calculate its sum. In this case, we can base on the following reasoning. The function corresponding to the series (6) or terms of the series obtained through its conversion should have a certain "shape," i.e., they must have one minimum and a repulsion part at $R \to 0$ and tend to zero at $R \to \infty$. Therefore, it is worth first regrouping Eq. (6) in the following way:

$$V_{\text{iso}}(R) = \frac{1}{R^6} \times$$

$$\times \left\{ \left(C_6(q) + \frac{C_7(q)}{R} \right) + \lambda \left(\frac{C_8(q)}{R^2} + \frac{C_9(q)}{R^3} \right) + \ldots \right\}. \quad (7)$$

Here λ is a formal parameter, which is assumed equal to unity in the final result. The converted series (7) must have correct asymptotic because of different signs of the coefficients $C_n(q)$ and $C_{n+1}(q)$.

Using then [0/1] Pade approximants for calculation of the sum of the series (7), we obtain:

$$V_{\text{iso}}^{[0/1]}(R) = \frac{1}{R^6} \frac{C_6(q) + \dfrac{C_7(q)}{R}}{1 + \dfrac{C_8(q)}{R^2} + \dfrac{C_9(q)}{R^3}} . \quad (8)$$

It can readily be shown that the isotropic part of the IMP in the form (8) has a correct asymptotic. The formally presented conversion of the series and its summation by Eq. (8) are equivalent to sequential application of Cesaro[12] and Pade[13] summation methods. In practical calculations, the coefficients $C_6(q)$, $C_7(q)$, ... can be estimated, for example, by representing the IMP as atom-atom potential.

Below we consider normal molecules, in which vibrations are small. Expand Eq. (8) in a power series over normal coordinates:

$$V_{\text{iso}}(R) = p_0(R) + \sum_i p_i(R)\, q_i + \sum_{ij} p_{ij}(R)\, q_i\, q_j + \ldots . \quad (9)$$

Here $p_0(R)$, $p_i(R)$, and $p_{ij}(R)$ are the coefficients consisting of the zero, first, and second derivatives of the coefficients C_i (i = 6, 7, 8, 9) from Eq. (8) with respect to the normal coordinates at the equilibrium configuration of a molecule. For example, the zero term of the series (9) is presented as

$$p_0 = (C_6^0)^2 \Big/ \left[R^6 \left(C_6^0 - \frac{C_7^0}{R} + \frac{C_8^0}{R^2} - \frac{C_9^0}{R^3} \right) \right].$$

From this equation we can see that the series (9) is alternate. Equations (8)–(9) determine the vibrational dependence of the isotropic part of the IMP. They can be used in Eqs. (1)–(3) for calculating the coefficients of pressure shift of spectral lines. On the other hand, the measured line shifts can be used for determining the coefficients of the expansion (9). Thus, according to Eqs. (1)–(3), the further task is to determine the matrix elements of the isotropic part of the IMP in different vibrational states. In this case, it is necessary to take into account intramolecular interactions that become dominating for the spectra in the near IR and visible regions.

Figure 1 illustrates the use of the derived equations by showing the isotropic part of the IMP calculated by Eq. (8). For calculation we took the following values of the coefficients C_n: $C_6 = -1$, $C_7 = 2$, $C_8 = -0.01$, $C_9 = 0.001$ (in atomic units). Such values of the coefficients C_n correspond to interaction of two He atoms.[8] We can see from the plot that Eq. (8) gives a correct asymptotic of the isotropic part of the IMP at both short ($R < 2$) and long ($R > 2$) separation. In Fig. 1, the area $R < 2$ corresponds to the repulsion part of the IMP, and the area $R > 2$ corresponds to the attraction.

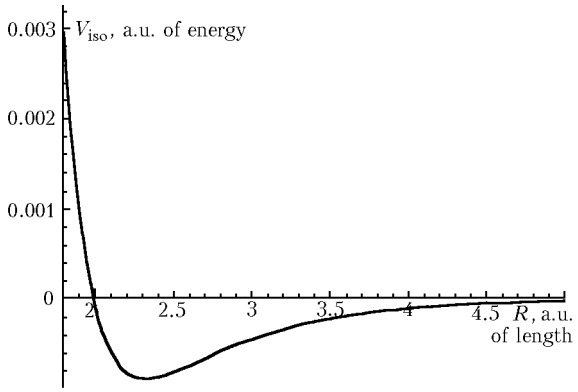

Fig. 1. [0/1] Pade approximant of the isotropic part of IMP as a function of the intermolecular separation R.

The dependence of the IMP on the vibrational excitation of the absorbing molecule was assessed in Ref. 4, in which the potential was presented as a sum of atom-atom potentials. The Lennard–Jones potential was used for coupled atom–atom potentials and its expansion into the Taylor series over vibrational coordinates was obtained. Numerical estimates[4] showed that the contribution to the line shift from the vibrational addition of the atom–atom potential for the 0–2 vibrational band of the HF molecule at collision with an Ar atom makes up about 11%.

Effective operator of the isotropic part of intermolecular potential

The isotropic part of the IMP $V_{iso}(R)$ depends on the intermolecular separation R and on the coordinates describing vibrations of nuclei of the colliding particles. The absorbing and distorting particles have different molecular characteristics (harmonic frequencies of vibrations, equilibrium rotational constants) and different parameters of smallness $\lambda = (2B_e/\omega_e)^{1/2}$. Therefore, the isotropic part of the IMP should be expanded in terms of nuclei shifts from the equilibrium positions in an absorbing molecule and a molecule-thermostat. The simplest way to solve this problem is to construct the effective operator of the isotropic part of the IMP by the method of contact transformations. The isotropic part $V_{iso}(R)$ can be expanded into a series over the normal coordinates in the form (9) with the coefficients being derivatives of $V_{iso}(R)$ with respect to the normal coordinates:

$$V_{iso}(R) = \sum_{n=6}^{\infty} \frac{C_n(q)}{R^n} = \sum_{m=1,2} \left\{ V_0^m(R) + \sum_{i=1}^{3N-6} \left(\frac{\partial V^m(R)}{\partial q_i} \right)_e q_i + \right.$$
$$\left. + \frac{1}{2} \sum_{i,j=1}^{3N-6} \left(\frac{\partial^2 V^m(R)}{\partial q_i \, \partial q_j} \right)_e q_i \, q_j + \ldots \right\}, \qquad (10)$$

where q_i are dimensionless normal coordinates; $(\partial^n V^m / \partial q_{i1} \, \partial q_{in})_e$ are derivatives of $V_{iso}(R)$ with respect to the normal coordinates at the equilibrium configuration of the absorbing molecule. It should be noted that $V_{iso}(R)$ is independent of the orientation of molecules, i.e., it is scalar, and therefore the coefficients in the series (10) are scalar too. Let us give the details of calculation of the effective operator of the isotropic part of the IMP $V_{iso}(R)$. The effect of anharmonicity of the vibrations of the nuclei of the colliding particles on $V_{iso}(R)$ was considered in the limiting scheme of ordering rotational-vibrational interactions that was called "overexcited oscillator" in Ref. 6. In this ordering scheme, the vibrational (H_{20}) and rotational (H_{02}) energies can be estimated by the following equations:

$$H_{20} \cong \chi^{\varepsilon} \, E_e \cong \chi^2 \, \chi^{-2+\varepsilon} \, E_e, \quad H_{02} \cong \chi^2 \, E_e \cong \chi^2 \, \omega_{vib}. \qquad (11)$$

Here E_e is the electronic energy of the first excited state; ω_{vib} is the typical molecular vibrational frequency; χ is the Born–Oppenheimer parameter; $\varepsilon \to 0$. It should be noted that the anharmonic part is separated automatically in expansion of the rotational-vibrational Hamiltonian H_{vr} of a quasi-rigid molecule only in this ordering scheme. That is, in the limiting scheme of "overexcited oscillator," H_{vr} can be represented in the form of an ordered sum:

$$H_{vr}^{(M)} = H_v + H'_{vr} = \sum_{m=1}^{\infty} \left(H_{m0} + \sum_{n=1}^{\infty} H_{mn}^{(M)} \right). \qquad (12)$$

Here the superscript (M) means the limiting scheme "overexcited oscillator," in which it is assumed that the purely vibrational energy achieves the values of the order of the electronic energy. In Eq. (12) $H_{10} = H_{11} = 0$. In the ordering scheme (M), vibrational contact transformations for the effective IMP operator are performed in terms of increasing powers of the vibrational variables, and unitary vibrational transformations of the method of contact transformations in the ordering scheme (M) have the form

$$U_M^{-1} = e^{-S_{30}} \, e^{-iS_{40}} \ldots e^{-iS_{21}} \, e^{-iS_{31}} \ldots e^{-iS_{12}} \, e^{-iS_{22}} \ldots . \qquad (13)$$

The transformed operator $V_{iso}(R)$ can be presented as a power series over vibrational operators:

$$\tilde{V}_{iso} = U_M^{-1} \, V_{iso} \, U_M = \sum_m (\tilde{V}_{iso})_m. \qquad (14)$$

To take into account the effect of anharmonicity in nuclei vibrations on $V_{iso}(R)$, the main part of this series can be approximated as

$$\tilde{V}_{iso} = (\tilde{V}_{iso})_{20} + (\tilde{V}_{iso})_{30} + (\tilde{V}_{iso})_{40} + \ldots . \qquad (15)$$

It should be kept in mind that the operators with even powers of the vibrational variables in Eq. (15) have both diagonal and off-diagonal elements in the basis of the Hamiltonian H_{20} (sets of harmonic oscillators of a molecule). The operators with odd powers of vibrational variables in Eq. (15) have only off-diagonal matrix elements in the basis of the Hamiltonian H_{20}, and the vibrational operators of power m in an assigned mode have matrix elements of the type $\langle v | v + m \rangle$, $\langle v | v + m - 2 \rangle$, $\ldots \langle v | v + 1 \rangle$. The part of the effective IMP operator $\langle V_{iso}(R) \rangle$ diagonal in the basis of the Hamiltonian H_{20} can be given by the equation

$$\langle \tilde{V}_{iso} \rangle \, H_{20} - H_{20} \, \langle \tilde{V}_{iso} \rangle = 0. \qquad (16)$$

The operator $(V_{iso}(R))_{20}$ transformed by the method of contact transformations can be expressed through commutators with the vibrational generator S_{30} in the form

$$(\tilde{V}_{iso})_{20} = (V_{iso})_{20} - i \, [S_{30}, (V_{iso})_{10}]. \qquad (17)$$

Let us give complete equations for the diagonal $\langle (V_{iso}(R))_{20} \rangle$ and off-diagonal $((V_{iso}(R))_{20})_{nd}$ parts through molecular constants and the expansion coefficients (10) – derivatives of $V_{iso}(R)$ with respect to the normal coordinates. For the diagonal part we have:

$$\langle(\tilde{V}_{\rm iso})_{20}\rangle = \sum_{i,j}\left\{\left(\frac{\partial^2 (V_i)_{10}}{\partial q_i\,\partial q_j}\right)_{\rm e} + \right.$$

$$\left. + \frac{1}{2}\sum_{i,j,m}\frac{\Phi_{ijm}}{\omega_m}\left(\frac{\partial (V_i)_{10}}{\partial q_i}\right)_{\rm e}\right\} a_i^{+1}\, a_i^{-1}\,\Delta_{ij}. \qquad (18)$$

And for the off-diagonal part

$$((\tilde{V}_{\rm iso})_{20})_{\rm nd} = \sum_{i,j,\sigma,\sigma'}\left\{\left(\frac{\partial^2 (V_i)_{10}}{\partial q_i\,\partial q_j}\right)_{\rm e} - \right.$$

$$- \sum_m \Phi_{ijm}\frac{\omega_m}{(\omega_i + \sigma\sigma'\omega_j)^2 - \omega_m^2}\times$$

$$\left.\times\left(\frac{\partial (V_i)_{10}}{\partial q_i}\right)_{\rm e}\right\} a_i^{\sigma}\, a_i^{\sigma'}\,(1 - \delta_{\sigma,-\sigma'})\,(1 - \Delta_{ij}). \qquad (19)$$

In Eqs. (18) and (19), we use the following designations: $a_i = q_i \pm ip_i$ are the ladder-type operators; $\sigma = \pm 1$; Φ_{ijm} are cubic constants of anharmonicity; ω_m are harmonic frequencies of the vibrations.

Let us consider some consequences following from the group-theory analysis of the series (10) and (15). The part $V_{\rm iso}(R)$ is a scalar value and under operations of symmetry group of a molecule, it transforms according to the totally symmetric representation. Consequently, the first term of the series (15) $(V_{\rm iso})_{10}$ contains only operators of totally symmetric coordinates. In other words, the coefficients in the first term of the series (10) for all symmetry groups of quasi-rigid molecules are derivatives with respect to the completely symmetric normal coordinates:

$$(V_{\rm iso})_{10} = \sum_{i \subset A_{1g}'}\left(\frac{\partial V_{\rm iso}}{\partial q_i}\right)_{\rm e} q_i. \qquad (20)$$

Summation is performed over all i belonging to the symmetry group A_{1g}'. The selection rule for determining non-zero coefficients in Eqs. (18) and (19), with the allowance made for the fact that $\Gamma(V_{\rm iso}) = A_{1g}'$, takes the form $[\Gamma_{\rm vib}^2] \subset A_{1g}'$, where $[\Gamma_{\rm vib}^2]$ means the symmetric square of a vibrational representation. Since $\Gamma_{\rm vib} = \sum_i^{\otimes}\Gamma_i$, where Γ_i are representations of the modes including in $\Gamma_{\rm vib}$, we have

$$[\Gamma_{\rm vib}^2] = \left[\left(\sum_i^{\otimes}\Gamma_i\right)^2\right] = \sum_i^{\otimes}[\Gamma_i] \oplus \sum_{ij}\Gamma_i \oplus \Gamma_j. \qquad (21)$$

In other words, the selection rule (20) breaks into a series of equations for irreducible representations of different modes (21).

Consider the part $\langle(V_{\rm iso}(R))\rangle$ diagonal in the basis of the Hamiltonian H_{20}:

$$\langle\tilde{V}_{\rm iso}\rangle = \langle\sum_m (\tilde{V}_{\rm iso})_{m0}\rangle = \langle(\tilde{V}_{\rm iso})_{20}\rangle + \langle(\tilde{V}_{\rm iso})_{40}\rangle + \ldots . \qquad (22)$$

The first diagonal [1/1] Pade approximant is written in the form

$$V_{\rm iso}^{[1/1]} = \frac{\langle(V_{\rm iso})_{20}\rangle^2}{\langle(V_{\rm iso})_{20}\rangle - \langle(V_{\rm iso})_{40}\rangle}. \qquad (23)$$

For triatomic molecules, the obtained equation can be written with the allowance for the matrix elements of the vibrational operators q:

$$V_{\rm iso}^{[1/1]} = \sum_{i=1,2,3}\frac{((V'_{\rm iso})_{20})^2\,(v_i + \frac{1}{2})}{(V'_{\rm iso})_{20} - (V'_{\rm iso})_{40}\,(v_i + \frac{1}{2})}. \qquad (24)$$

It should be noted that Eq. (24) is similar to the [1/1] Pade approximant for medium polarizability describing its dependence on the vibrational quantum numbers for quasi-rigid molecules like H_2O (Ref. 11). For diatomic molecules having only one vibration, $i = 1$, $v_i = v$. Thus, we have obtained asymptotic estimates for the infinite series of the effective operator of the isotropic part of IMP in the form of the first diagonal Pade approximant. Using Eqs. (23) and (24), we can calculate the sum of the IMP series with diagonal matrix elements $V_{\rm iso}(R)$ found in Ref. 4 for diatomic and triatomic molecules with the Lennard–Jones atom–atom potential.

Conclusion

In this paper, we have obtained asymptotic estimates in the form of the first Pade approximant for infinite series of two types. Equation (8) is an asymptotic estimate of the isotropic part of IMP with the coefficients C_n dependent on the vibrational coordinates q. The [0/1] Pade approximant has been derived for the isotropic part of the IMP; it correctly describes the asymptotic as the intermolecular separation varies within $0 < R < 5$ (see Fig. 1). Equation (24) is an asymptotic estimate in the form of the [1/1] Pade approximant for the effective operator of the isotropic part of the IMP with the explicit dependence on the vibrational quantum number.

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