

Excited states in the limit of large dimensionality

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I. INTRODUCTION

The limit of large dimensionality was studied by Loeser [1] for a general case of N -electron atom, where two coefficients of $1/D$ series were derived. Using analytic expressions constructed on the basis of two terms of $1/D$ -expansion, Loeser calculated ground state energies of all atoms with accuracy of order of 1%. On another hand, the $1/D$ -expansion for hydrogen atom was known to be convergent for $D > 1$, and the first three terms of $1/D$ -expansion for helium atom show the convergence similar to the hydrogen atom [2, 3]. Thus, Mlodinow and Papanicolaou [2] pointed out that the accuracy for $D = 3$ can be improved by including higher terms of the series. Mlodinow and Papanicolaou [2] were able to calculate the first anharmonic correction going beyond a simple harmonic approximation. However, their method [4] which was originally used in $1/N$ -expansion in statistical physics is less convenient for calculating higher order terms of the $1/D$ series. A simpler approach resembling analysis of normal modes in the theory of molecular vibrations was adopted in

[5, 6, 9]. Goodson adjusted this method for computer coding and derived recursive relations suitable for calculation of any order of $1/D$ -expansion, firstly for the ground state of helium [9], and later for excited S-states [7]. He found that the series is factorially divergent, and that Pade approximants could accurately sum the series [8]. A similar approach was used to calculate higher orders of $1/D$ -expansion for two-electron atoms [16] and for different three-body models [17].

Here, we systematically review and re-derive the results published in the paper [7]. It should be noted that “moment method” [18, 19] of calculation of terms of $1/D$ -expansion used in this paper and in the earlier paper [9] was substituted in later publications [8, 10] by a more efficient “matrix method” developed by Dunn [14], which has an additional advantage of being equally useful both for the ground and excited states. “Matrix method” differ from “moment method” in choice of auxiliary parameters entering recurrence relations. In “moment method”, the relations are derived for expectation values of powers of coordinate operators, while in “matrix method” they are derived for components of the wave function in the harmonic oscillator basis set. “Matrix method” is based on applying Green’s function for calculating successive orders of perturbation theory. It was used for similar problems in [16, 17]. Here, we focus on the “matrix method” described in a later paper [14], dropping the “moment method” as it may be now only of historical interest.

First, we consider the large- D limit for S-states of a hydrogen atom and compare convergence of the series for ground vs. excited states. Then, we describe the method of calculation and consider numerical results for the ground and excited states of helium atom. We analyze several factors affecting convergence and discuss results of Pade-summation and divergence of the asymptotic series in $1/D$.

II. GROUND AND EXCITED STATES OF A HYDROGEN ATOM IN LARGE-DIMENSIONAL LIMIT

Energy of S-state of a hydrogen atom is given by generalization of Rydberg formula [20],

$$E = -\frac{2}{(D-1+2n_r)^2}, \quad (1)$$

where n_r is a number of nodes of the radial wave function, which is also known as “radial quantum number”.

For the ground state, $n_r = 0$, and the $1/D$ -expansion is

$$E = -\frac{2}{(D-1)^2} = 2D^{-2}\left(1 + \frac{2}{D} + \frac{3}{D^2} + \dots\right), \quad (2)$$

The series (2) has radius of convergence 1. For excited states,

$$E = -\frac{2}{(D-1+2n_r)^2} = 2D^{-2} \sum_{k=0}^{\infty} (2n_r-1)^k \frac{(-1)^k (k+1)}{D^k}, \quad (3)$$

and the radius of convergence is $1/(2n_r-1)$. Thus, the series could be summed for the ground and the first excited state for $D=3$, but it diverges for higher excited states. Since the functional form of the energy is a rational function of $1/D$, the series could be summed for any excited state using Pade approximants $[m/n]$ with $n \geq 2$, where Pade approximant $[m/n]$ is defined as a ratio of two polynomials of degrees m and n that equals to the function to be approximated up to the order $m+n$ in $1/D$.

III. SCHRÖDINGER EQUATION FOR D -DIMENSIONAL TWO-ELECTRON ATOMS

D -dimensional generalization of Schrödinger equation for helium-like atoms reads

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} - E\right) \Psi(\mathbf{r}_1, \mathbf{r}_2) = 0, \quad (4)$$

where $\mathbf{r}_1, \mathbf{r}_2$ are vectors in D -dimensional space, ∇_1, ∇_2 are D -dimensional Laplacians, $r_1 = |\mathbf{r}_1|, r_2 = |\mathbf{r}_2|, r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. In equation (4), Ψ is the wavefunction, which is a function of $2D$ components of vectors $\mathbf{r}_1, \mathbf{r}_2$, E is energy, Z is nuclear charge. We use atomic units where electron mass, charge, and Plank's constants are equal to one. A part of the expression (4) containing second derivatives is called kinetic energy term,

$$T\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2}\right) \Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (5)$$

and a part containing coordinates is called potential term,

$$V\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (6)$$

We use approximation of infinitely heavy nucleus, so that the kinetic term does not contain derivatives in respect to coordinates of the nucleus. Goodson [7] wrote Schrödinger equation in different units, where nuclear charge instead of electron charge is one. In his notations, the potential is $-1/r_1 - 1/r_2 + \lambda/r_{12}$, where $\lambda = 1/Z$.

IV. WAVE FUNCTIONS OF S-STATES EXPRESSED IN INTERNAL COORDINATES

Here, we consider a linear subspace of functions of two D -dimensional vectors that could be expressed as a function of only three arguments,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(|\mathbf{r}_1|, |\mathbf{r}_2|, |\mathbf{r}_1 - \mathbf{r}_2|), \quad (7)$$

It is a generalization of “S-state”, or a state with zero angular momentum, to the space of D dimensions. If we define a tensor of angular momentum in D -dimensional space as

$$L_{ij} = \frac{\hbar}{i} \left(r_{1i} \frac{\partial}{\partial r_{1j}} + r_{2i} \frac{\partial}{\partial r_{2j}} - r_{1j} \frac{\partial}{\partial r_{1i}} - r_{2j} \frac{\partial}{\partial r_{2i}} \right), \quad (8)$$

then $L_{ij}\Psi = 0$ for any i and j .

Let us rewrite the Schrödinger equation in three internal coordinates,

$$r_1 = |\mathbf{r}_1|, \quad r_2 = |\mathbf{r}_2|, \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|. \quad (9)$$

Here, we use the approach described earlier in notes about Loeser’s papers. Expressing Laplacian through derivatives in respect to inter-particle distances according to equa-

tion (??), we obtain

$$\begin{aligned}
T &= -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) \\
&= -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2 \frac{\partial^2}{\partial r_{12}^2} + 2 \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} + 2 \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right. \\
&\quad \left. + \frac{D-1}{r_1} \frac{\partial}{\partial r_1} + \frac{D-1}{r_2} \frac{\partial}{\partial r_2} + 2 \frac{D-1}{r_{12}} \frac{\partial}{\partial r_{12}} \right). \tag{10}
\end{aligned}$$

The scaling transformation $P = S^{(D-1)/2} \psi$ where

$$S = \frac{1}{4} (2r_1^2 r_{12}^2 + 2r_{12}^2 r_2^2 + 2r_1^2 r_2^2 - r_1^4 - r_2^4 - r_{12}^4)^{1/2} \tag{11}$$

is the area of a triangle with the sides r_1 , r_2 , r_{12} , removes from equation (10) the terms linear in derivatives. The D -dimensional Schrödinger equation reduces to the form

$$\begin{aligned}
&\left(-\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right. \\
&\quad \left. + V_{\text{eff}}(r_1, r_2, r_{12}) - E \right) P(r_1, r_2, r_{12}) = 0, \tag{12}
\end{aligned}$$

where

$$V_{\text{eff}}(r_1, r_2, r_{12}) = \frac{(D-1)^2}{32} \frac{r_1^2 + r_2^2}{S^2(r_1, r_1, r_{12})} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}. \tag{13}$$

V. LIMIT OF $D \rightarrow \infty$

Derivations are similar to those for harmonic oscillator, see previous notes about “two papers”. First, we make scaling transformation of variables, $r_1 \rightarrow \tilde{r}_1 = D^{1/2} r_1$, $r_2 \rightarrow \tilde{r}_2 = D^{1/2} r_2$, $r_{12} \rightarrow \tilde{r}_{12} = D^{1/2} r_{12}$, and rewrite equation (12) in the form

$$\begin{aligned}
&\left(-\frac{1}{2D^2} \frac{\partial^2}{\partial \tilde{r}_1^2} - \frac{1}{2D^2} \frac{\partial^2}{\partial \tilde{r}_2^2} - \frac{1}{D^2} \frac{\partial^2}{\partial \tilde{r}_{12}^2} - \frac{1}{D^2} \frac{\tilde{r}_1^2 + \tilde{r}_{12}^2 - \tilde{r}_2^2}{\tilde{r}_1 \tilde{r}_{12}} \frac{\partial^2}{\partial \tilde{r}_1 \partial \tilde{r}_{12}} - \frac{1}{D^2} \frac{\tilde{r}_2^2 + \tilde{r}_{12}^2 - \tilde{r}_1^2}{\tilde{r}_2 \tilde{r}_{12}} \frac{\partial^2}{\partial \tilde{r}_2 \partial \tilde{r}_{12}} \right. \\
&\quad \left. + U(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) - \tilde{E} \right) \tilde{P}(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = 0, \tag{14}
\end{aligned}$$

where

$$U(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = \frac{1}{32} \left(1 - \frac{1}{D} \right)^2 \frac{\tilde{r}_1^2 + \tilde{r}_2^2}{S^2(\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12})} - \frac{1}{\tilde{r}_1} - \frac{1}{\tilde{r}_2} + \frac{\lambda}{\tilde{r}_{12}}. \tag{15}$$

We expand the potential U in powers of $1/D$,

$$U = U_0 + \frac{1}{D}U_1 + \frac{1}{D^2}U_2, \quad (16)$$

where

$$U_0(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = \frac{1}{32} \frac{\tilde{r}_1^2 + \tilde{r}_2^2}{S^2(\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12})} - \frac{1}{\tilde{r}_1} - \frac{1}{\tilde{r}_2} + \frac{\lambda}{\tilde{r}_{12}}, \quad (17)$$

$$U_1(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = \frac{1}{16} \frac{\tilde{r}_1^2 + \tilde{r}_2^2}{S^2(\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12})}, \quad (18)$$

$$U_2(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = \frac{3}{32} \frac{\tilde{r}_1^2 + \tilde{r}_2^2}{S^2(\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12})}. \quad (19)$$

It will be proven in the next section that the large D limit of energy of some quantum-mechanical state is expressed through a minimum of the potential U_0 ,

$$E \sim \frac{1}{D^2} \tilde{E}_0, \quad \tilde{E}_0 \equiv \min_{\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12}} U_0(\tilde{r}_1, \tilde{r}_1, \tilde{r}_{12}). \quad (20)$$

Here, we use non-rigorous “heuristic” argument to derive equation (20) for the ground state. In equation (14), the parameter $1/D$ formally plays the role of Planck’s constant, because its square stands as a factor in front of second derivatives. It means that the limit $D \rightarrow \infty$ corresponds to the classical mechanics in the potential $U_0 = \lim_{D \rightarrow \infty} U$. In this limit, the ground state turns into a classical state with the lowest energy, which is a static state of a particle resting at the minimum of the potential U_0 .

Minimum of the potential U_0 could be either symmetric, $r_1 = r_2$ or asymmetric, $r_1 \neq r_2$. For a neutral atom of helium and all positive ions $Z \geq 2$ only the former a symmetric minimum is possible, see Appendix,

$$r_1^{(0)} = r_2^{(0)} = \frac{1}{4(1+c)^2}, \quad (21)$$

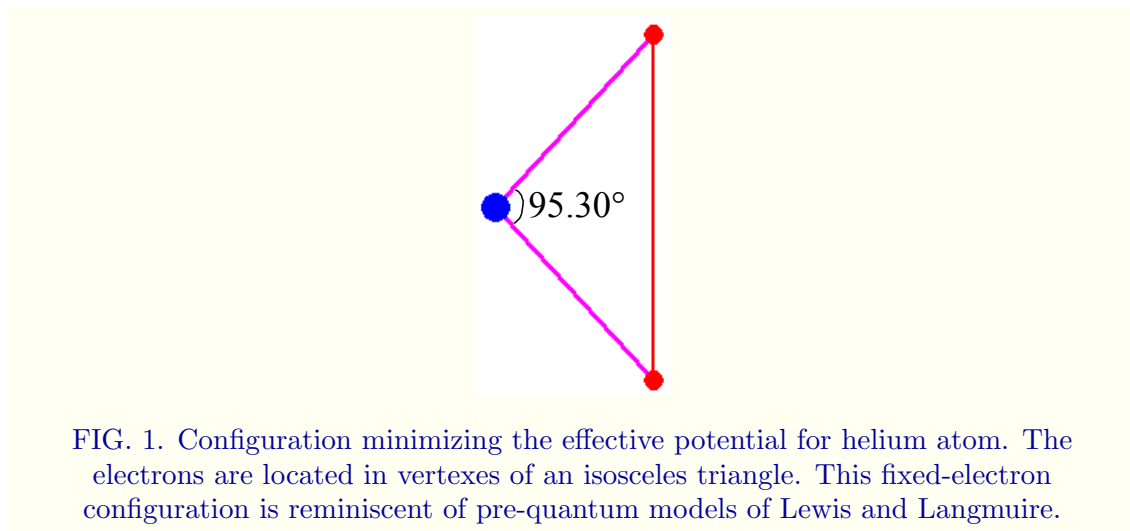
$$r_{12}^{(0)} = \frac{\sqrt{1-c}}{2\sqrt{2}(1+c)^2}, \quad (22)$$

where

$$c = -(\lambda/8)^2 - (\lambda/8)(2 + \lambda^2/64)^{1/2}. \quad (23)$$

For the case of helium atom the minimal configuration is an isosceles triangle sgown on

Fig. 1. Finding of an asymmetric minimum reduces to solving of a seventh degree polynomial



equation, see Appendix. These minima exist only in a narrow range of $0.809585 < \lambda < 1$ corresponding to hypothetical fractional nuclear charge $1 < Z < 1.2352$. In general, there are four possible cases (see Fig 2): (1) minima are asymmetric, (2) minima are asymmetric, with existence of a local symmetric secondary minimum (above the global asymmetric minimum), (3) minimum is symmetric, with two flanking secondary asymmetric minima, (4) a single symmetric minimum, with existence of two asymmetric complex stationary points. A neutral helium atom ($Z = 2$) and all positive ions ($Z \geq 3$) belong to the case (4), with only one symmetric minimum.

VI. FIRST-ORDER CORRECTIONS, OR “LANGMUIR VIBRATIONS”

Here, we consider the problem by approximating the potential by a parabola and solving the quantum equation for a harmonic oscillator. It should be noted that although it corrects the classical limit, equation (20), by first-order term $\sim 1/D$, this approximation is in fact the zero-order quantum approximation in a subsequent anharmonic perturbation theory rather than “correction” to the classical limit. It is a consequence of the fact that the classical limit is essentially different from the quantum problem, so it cannot be considered by itself as zero-order approximation for developing the series in $1/D$. Indeed, in the classical limit the wave function squared tends to an infinitely sharp distribution (delta-function) concentrated around the minimum of the potential which is qualitatively different from smooth wave functions for finite values of D . Physicist refer to this case as “singular” limit.

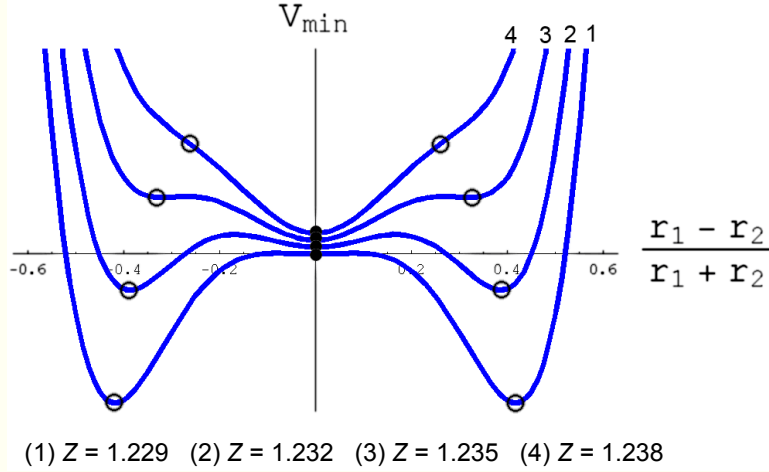


FIG. 2. Shape of the effective potential for helium-like ions in the direction of soft antisymmetric mode. V_{\min} is the minimum of V_{eff} for the given value of the parameter of asymmetry, $\frac{r_1 - r_2}{r_1 + r_2}$. The charge Z is related to the Coulomb force parameter λ as $\lambda = 1/Z$. Curves for different values of Z are shifted along the vertical axis for easier plotting.

Let us introduce new variables (x, y, z) instead of old variables $(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12})$,

$$\tilde{r}_1 = \tilde{r}_1^{(0)} + D^{-1/2}x, \quad (24)$$

$$\tilde{r}_2 = \tilde{r}_2^{(0)} + D^{-1/2}y, \quad (25)$$

$$\tilde{r}_{12} = \tilde{r}_{12}^{(0)} + D^{-1/2}z. \quad (26)$$

Then, equation (14) could be rewritten in new variables as

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} - \frac{\tilde{r}_1^2 + \tilde{r}_{12}^2 - \tilde{r}_2^2}{\tilde{r}_1 \tilde{r}_{12}} \frac{\partial^2}{\partial x \partial z} - \frac{1}{D^2} \frac{\tilde{r}_2^2 + \tilde{r}_{12}^2 - \tilde{r}_1^2}{\tilde{r}_2 \tilde{r}_{12}} \frac{\partial^2}{\partial y \partial z} \right) + v(x, y, z) - \epsilon) Y(x, y, z) = 0, \quad (27)$$

where $Y(x, y, z) = \tilde{P}(\tilde{r}_1^{(0)} + D^{-1/2}x, \tilde{r}_2^{(0)} + D^{-1/2}y, \tilde{r}_{12}^{(0)} + D^{-1/2}z)$ is a scaled wavefunction and $\epsilon = D\tilde{E}$ is the scaled energy. The potential in equation (27) is ...

... (will be added more sections)

Excited S-states of helium could be treated in the same way as the ground state, but using non-zero quantum numbers in the harmonic vibrational modes [7, 9]. Calculations require only finite number of arithmetic operations for each order in $1/D$, but they require large amount of computer resources, since memory grows $\sim k^4$ and processor time $\sim k^8$, where

k is the order in $1/D$. In addition, calculations are numerically unstable, so that precision decreases approximately ten times as k increases by one. Goodson et al. [12] devised a more economical “matrix method” which is less demanding in processor time, and calculated 30 terms of the series for the ground state. This method was later used for lowest excited states [7], where it allows to calculate more than 20 terms. Basically the same algorithm on modern computers with multiple-precision arithmetic allows to calculate up to 50 terms. Table VI lists coefficients of $1/D$ expansion $E = D^{-2}(E_0 + E_1/D + E_2/D^2 + \dots)$ for the ground and two lowest excited states of helium. Unlike coefficients with decreasing number of significant figures given in [7, 12], here all coefficients are given with the same number of significant figures. Coefficients were obtained with accuracy of at least 100 significant figures, because we used multiple-precision arithmetic with an excessive accuracy of 200 figures.

Cauchy root test ($|E_k/E_0|^{1/k}$) shows [7] that $|E_k/E_0|^{1/k} \rightarrow \infty$ as $k \rightarrow \infty$ which means that radius of convergence of the series is zero. Numerical study of Borel transformation of the series [12] gives the behavior of the coefficients at large order as

$$E_k \sim k^\beta \operatorname{Re}(ca^k)k!, \quad (28)$$

where c and a are some complex-valued constants, and β is a real constant. For the ground state, $a^{-1} = -0.32362 + 0.10054i$, $\beta = -1/2$. and for $1s2s^3S$ excited state $a^{-1} = -0.308 + 0.108i$, although some theoretical studies indicate that a should be the same for all states. For $1s2s^1S$ the series is strongly divergent because of so-called effect of Fermi resonance...

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- [1] J. G. Loeser, J. Chem. Phys. **86**, 5635 (1987).
 - [2] L. D. Mlodinow and N. Papanicolaou, Ann. Phys. **131**, 1 (1981).
 - [3] E. Witten, Phys. Today, July, 38 (1980).
 - [4] L. D. Mlodinow. The large N expansion in quantum mechanics. Dissertation, Berkeley, 1981.
 - [5] P. du T. van der Merwe, J. Chem. Phys. **81**, 5976 (1984).
 - [6] A. A. Belov and Yu. E. Lozovik, Phys. Lett. A **142**, 389 (1989).
 - [7] D. Z. Goodson and D. K. Watson, Phys. Rev. A **48**, 2668 (1993).
 - [8] D. Z. Goodson, in *Dimensional Scaling in Chemical Physics*, p. 359 (1993).

TABLE I. Coefficients of the $1/D$ -expansion of the energy of the ground $1s^2^1S$ and $1s2s^3S$, $1s2s^1S$ excited states of helium. Energies are divided by $Z^2 = 4$ for easier comparison with tables in [7, 12].

k	$1s^2^1S$	$1s2s^3S$	$1s2s^1S$
	E_k	E_k	E_k
0	$-0.273\,776\,914\,112\,772 \cdot 10^1$	$-0.273\,776\,914\,112\,772 \cdot 10^1$	$-0.273\,776\,914\,112\,772 \cdot 10^1$
1	$-0.605\,759\,194\,836\,365 \cdot 10^1$	$-0.250\,856\,408\,180\,831 \cdot 10^1$	$-0.631\,212\,358\,902\,951 \cdot 10^0$
2	$-0.886\,218\,378\,983\,332 \cdot 10^1$	$-0.803\,530\,933\,369\,665 \cdot 10^1$	$-0.415\,806\,497\,802\,236 \cdot 10^2$
3	$-0.139\,006\,372\,818\,208 \cdot 10^2$	$-0.217\,406\,297\,785\,584 \cdot 10^1$	$0.924\,638\,517\,825\,852 \cdot 10^3$
4	$-0.543\,672\,043\,287\,805 \cdot 10^1$	$-0.733\,985\,737\,832\,461 \cdot 10^2$	$-0.396\,416\,185\,364\,982 \cdot 10^5$
5	$-0.827\,394\,676\,588\,397 \cdot 10^2$	$0.918\,913\,732\,804\,691 \cdot 10^3$	$0.213\,025\,950\,728\,081 \cdot 10^7$
6	$0.131\,269\,893\,398\,517 \cdot 10^3$	$-0.152\,292\,462\,835\,742 \cdot 10^5$	$-0.129\,651\,001\,399\,477 \cdot 10^9$
7	$0.101\,260\,076\,492\,362 \cdot 10^5$	$0.275\,970\,825\,487\,888 \cdot 10^6$	$0.849\,480\,470\,121\,711 \cdot 10^{10}$
8	$-0.433\,338\,867\,474\,867 \cdot 10^6$	$-0.543\,499\,063\,189\,321 \cdot 10^7$	$-0.584\,311\,304\,054\,813 \cdot 10^{12}$
9	$0.142\,144\,642\,644\,793 \cdot 10^8$	$0.112\,004\,529\,756\,752 \cdot 10^9$	$0.416\,050\,786\,221\,958 \cdot 10^{14}$
10	$-0.443\,814\,218\,443\,243 \cdot 10^9$	$-0.227\,691\,999\,243\,618 \cdot 10^{10}$	$-0.304\,019\,175\,709\,726 \cdot 10^{16}$
11	$0.138\,213\,439\,984\,308 \cdot 10^{11}$	$0.396\,766\,902\,942\,189 \cdot 10^{11}$	$0.226\,682\,537\,645\,016 \cdot 10^{18}$
12	$-0.433\,011\,023\,588\,743 \cdot 10^{12}$	$-0.228\,448\,804\,542\,042 \cdot 10^{12}$	$-0.171\,773\,965\,895\,695 \cdot 10^{20}$
13	$0.135\,235\,142\,263\,286 \cdot 10^{14}$	$-0.323\,649\,810\,503\,408 \cdot 10^{14}$	$0.131\,902\,342\,310\,846 \cdot 10^{22}$
14	$-0.409\,599\,384\,963\,817 \cdot 10^{15}$	$0.277\,018\,578\,410\,563 \cdot 10^{16}$	$-0.102\,412\,397\,582\,321 \cdot 10^{24}$
15	$0.112\,287\,235\,940\,352 \cdot 10^{17}$	$-0.170\,660\,303\,123\,796 \cdot 10^{18}$	$0.802\,647\,117\,345\,928 \cdot 10^{25}$
16	$-0.216\,308\,554\,547\,690 \cdot 10^{18}$	$0.948\,351\,712\,932\,780 \cdot 10^{19}$	$-0.634\,150\,205\,854\,848 \cdot 10^{27}$
17	$-0.322\,430\,439\,975\,667 \cdot 10^{19}$	$-0.502\,447\,417\,404\,554 \cdot 10^{21}$	$0.504\,536\,825\,841\,155 \cdot 10^{29}$
18	$0.788\,061\,799\,083\,826 \cdot 10^{21}$	$0.257\,694\,378\,021\,768 \cdot 10^{23}$	$-0.403\,878\,561\,296\,888 \cdot 10^{31}$
19	$-0.699\,028\,626\,681\,805 \cdot 10^{23}$	$-0.127\,445\,428\,579\,623 \cdot 10^{25}$	$0.325\,054\,216\,150\,535 \cdot 10^{33}$
20	$0.507\,872\,349\,910\,954 \cdot 10^{25}$	$0.593\,683\,321\,341\,119 \cdot 10^{26}$	$-0.262\,874\,891\,025\,081 \cdot 10^{35}$
21	$-0.339\,035\,331\,840\,671 \cdot 10^{27}$	$-0.243\,809\,976\,442\,846 \cdot 10^{28}$	$0.213\,507\,202\,365\,113 \cdot 10^{37}$
22	$0.215\,074\,794\,023\,052 \cdot 10^{29}$	$0.684\,491\,805\,883\,434 \cdot 10^{29}$	$-0.174\,084\,626\,217\,402 \cdot 10^{39}$
23	$-0.130\,512\,242\,138\,343 \cdot 10^{31}$	$0.154\,206\,214\,617\,566 \cdot 10^{31}$	$0.142\,440\,495\,440\,181 \cdot 10^{41}$
24	$0.748\,745\,440\,244\,603 \cdot 10^{32}$	$-0.516\,869\,644\,621\,971 \cdot 10^{33}$	$-0.116\,921\,395\,846\,615 \cdot 10^{43}$
25	$-0.390\,344\,292\,918\,235 \cdot 10^{34}$	$0.635\,198\,931\,932\,558 \cdot 10^{35}$	$0.962\,547\,378\,366\,071 \cdot 10^{44}$
26	$0.163\,196\,213\,464\,029 \cdot 10^{36}$	$-0.631\,280\,989\,395\,567 \cdot 10^{37}$	$-0.794\,534\,740\,139\,634 \cdot 10^{46}$
27	$-0.218\,372\,826\,550\,928 \cdot 10^{37}$	$0.569\,077\,082\,811\,314 \cdot 10^{39}$	$0.657\,466\,887\,593\,857 \cdot 10^{48}$
28	$-0.636\,894\,003\,577\,323 \cdot 10^{39}$	$-0.481\,648\,551\,452\,523 \cdot 10^{41}$	$-0.545\,284\,648\,793\,546 \cdot 10^{50}$
29	$0.112\,773\,820\,419\,316 \cdot 10^{42}$	$0.385\,620\,740\,525\,774 \cdot 10^{43}$	$0.453\,198\,293\,824\,880 \cdot 10^{52}$
30	$-0.137\,820\,805\,524\,465 \cdot 10^{44}$	$-0.288\,913\,059\,529\,396 \cdot 10^{45}$	$-0.377\,401\,692\,387\,661 \cdot 10^{54}$

[9] D. Z. Goodson and D. R. Herschbach, Phys. Rev. Lett. **58**, 1628 (1987).

[10] D. Z. Goodson, M. López-Cabrera, D. R. Herschbach, and J. D. Morgan III, J. Chem. Phys. **97**, 8481 (1992).

[11] D. Z. Goodson, D. K. Watson, J. G. Loeser, and D. R. Herschbach, Phys. Rev. A **44**, 97 (1991).

[12] D. Z. Goodson, M. López-Cabrera, D. R. Herschbach, and J. D. Morgan III, Phys. Rev. A

- 97**, 92 (1992).
- [13] D. K. Watson and D. Z. Goodson, *Phys. Rev. A* **51**, R5 (1995).
- [14] M. Dunn et al., *J. Chem. Phys.* **101**, 5987 (1994).
- [15] D. K. Watson, M. Dunn, T. C. Germann, D. R. Herschbach, D. Z. Goodson, and J. R. Walkup, *New Methods in Quantum Theory*, edited by C. A. Tsipis, V. S. Popov, D. R. Herschbach, and J. Avery, NATO Conference Book, Vol. 8 (Kluwer Academic, Dordrecht, Holland, 1996).
- [16] Sergeev A. V., Abstracts of All-Union Conference on the Theory of Atoms and Atomic Spectra. Minsk, 1983, p. 66 (in Russian).
- [17] Sergeev A. V., *Sov. J. of Nucl. Phys.* **50**, 589, (1989)
- [18] J. P. Ader, *Phys. Lett.* **97A**, 178, (1983)
- [19] F. M. Fernandez, J. F. Ogilvie, and R. H. Tipping, *J. Phys. A: Math. Gen.* **20**, 3777, (1987)
- [20] D. R. Herschbach, in *Dimensional Scaling in Chemical Physics*, p. 7 (1993).