Four-parameter exactly solvable potential for diatomic molecules

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A four-parameter potential function is introduced for bond-stretching vibration of diatomic molecules. It may fit the experimental RKR (Rydberg-Klein-Rees) curve more closely than the Morse function, especially when the potential domain extends to near the dissociation limit. The corresponding Schrödinger equation is solved exactly for zero total angular momentum and approximately for nonzero total angular momentum.

I. INTRODUCTION

In recent years the large-amplitude vibration of molecules has received significant attention.[1-4] For bond-stretching vibration, investigators often use the Morse potential[5]

$$U_M(r) = D_e[1 - e^{-a(r-r_e)}]^2 , \qquad (1)$$

where D_e is the dissociation energy, r_e is the equilibrium bond length, and

$$k_e = 2D_e a^2 = U'''(r_e) \qquad (2)$$

is the force constant, which is related to the equilibrium angular frequency ω_e and reduced mass μ by the Dunham formula

$$k_e = \mu \omega_e^2 . \qquad (3)$$

The Morse potential has better large-amplitude behavior than the harmonic-oscillator potential. Using the Morse wave functions as a basis one achieves a fast convergence in the calculation, e.g., diagonalization of a Hamiltonian.

However, the Morse function still shows a large deviation from the experimental curve. In Ref. 6 comparisons for 19 states of diatomic molecules give that the average absolute deviation of the Morse function from the Rydberg-Klein-Rees (RKR) curve[7] is 3.68%. In addition, Varshni and Levine have proposed the potential functions

$$U_V(r) = D_e \left[1 - \frac{r_e}{r} e^{-b_V(r^2 - r_e^2)} \right]^2 \qquad (4)$$

and

$$U_L(r) = D_e \left[1 - \frac{r_e}{r} e^{-b_L(r^p - r_e^p)} \right]^2 , \qquad (5)$$

where

$$p = 2 + \tfrac{1}{4}(\Delta^{1/2} - 4)(\Delta^{1/2} - 2)/(\Delta^{1/2} - 1) ,$$

$$b_V = \tfrac{1}{2}(\Delta^{1/2} - 1)/r_e^2 ,$$

$$\Delta^{1/2} = ar_e , \qquad (6)$$

$$b_L = p^{-1}(\Delta^{1/2} - 1)/r_e^p .$$

The average absolute deviation of these two functions decrease to 2.31% and 1.99%, respectively. However, the Schrödinger equation for these two potentials can hardly be solved exactly.

Moreover, when the domain of the potential extends to near the dissociation limit, the deviations of these three functions from the RKR curve become very large. Table I shows that the deviations of Morse, Varshni, and Levine functions reach about 50%, 34%, and 37% at $r = 3.49$ Å for the $X\,^1\Sigma_g^+$ state of Cs_2, and in the domain from 3.49 to 11.53 Å the mean absolute deviations are 16.1%, 10.3%, and 11.4%, which are still very large. In Table II are collected the mean absolute deviations of 15 molecular states from the RKR curves. The domains of the potentials are indicated by the E_{max}/D_e column where E_{max} is the highest level in the RKR turning points. Another series of calculations[27] give that the mean-square deviations are 30–60 % more than the mean absolute deviations in Table II. It shows that for the most states the deviations of the Morse potential become very large when we consider a large-domain potential.

II. FOUR-PARAMETER POTENTIAL

Now we introduce a potential function

$$U(r) = D_e \left[\frac{1 - e^{-b(r-r_e)}}{1 - ce^{-b(r-r_e)}} \right]^2 , \quad |c| < 1 \qquad (7)$$

with

$$b = a(1 - c) . \qquad (8)$$

Just as in the above three potentials, it satisfies Eqs. (2), (3), and

$$U(r_e) = U'(r_e) = 0, \quad U(\infty) = D_e . \qquad (9)$$

The higher-order derivations are

$$U'''(r_e) = -6D_e(1 + c)a^3 = (1 + c)U_M'''(r_e) , \qquad (10)$$

$$U^{(4)}(r_e) = 2D_e a^4 (7 + 22c + 7c^2)$$

$$= (1 + \tfrac{22}{7}c + c^2)U_M^{(4)}(r_e) . \qquad (11)$$

This means that the above four functions have the same

TABLE I. Deviations from the experimental RKR curves of four potentials: U_M, Morse; U_V, Varshni; U_L, Levine; U, the four-parameter potential in this work. The parameter c is determined by minimizing the mean absolute deviation of U from U_{RKR} and is listed in Table II.

Molecular state	n	r (Å)	U_{RKR} (cm^{-1})	$U_M - U_{RKR}$ (cm^{-1})	$U_V - U_{RKR}$ (cm^{-1})	$U_L - U_{RKR}$ (cm^{-1})	$U - U_{RKR}$ (cm^{-1})
Cs$_2$ $X\ ^1\Sigma_g^+$	137	3.492 28	3629.099	1813.3	1224.5	1348.97	−24.32
	120	3.508 79	3512.575	1707.72	1151.32	1268.75	−24.27
	80	3.615 06	2772.466	1179.58	799.47	878.93	16.45
	40	3.842 21	1559.92	462.35	313.12	343.79	23.53
	0	4.5408	20.981	0.56	0.37	0.41	0.08
	0	4.7607	20.981	−0.52	−0.34	−0.38	−0.09
	40	5.978 07	1559.92	−242.36	−145.36	−163.51	−76.69
	80	7.007 17	2772.466	−414.07	−213.19	−248.35	−151.03
	120	8.963 29	3512.575	−224.48	−48.43	−72.97	−61.1
	137	11.532 16	3629.099	−42.25	10.52	6.43	−0.09
I$_2$ XO_g^+	108	2.268 67	12 543.9343	2462.22	727.65	346.59	−42.93
	90	2.271 14	12 340.1776	2404.09	712.6	340.74	−35.93
	60	2.297 98	10 272.6273	1843.11	566.2	283.43	25.36
	30	2.370 18	5932.678	823.24	273.93	150.03	69.94
	0	2.618 39	107.0981	2.1	0.88	0.6	0.65
	0	2.718 04	107.0981	−2.1	−0.94	−0.66	−0.8
	30	3.218 79	5932.678	−766.98	−392.16	−301.4	−454.8
	60	3.696	10 272.6273	−1157.5	−483.68	−332.68	−708.48
	90	4.938 31	12 340.1776	−158.75	96.31	127.37	−25
	108	9.0775	12 543.9343	3.23	3.4	3.4	3.36
ICl $A'\ ^3\Pi_2$	38	2.306	4803.73	967.61	320.69	104.83	−100.93
	30	2.312	4539.68	963.94	359.61	157.54	−31.64
	20	2.34	3664.63	711.22	276.65	129.95	4.29
	10	2.404	2134.22	308.67	122.02	57.73	14.35
	0	2.596	111.85	0.79	−1.17	−1.88	−1.99
	0	2.744	111.85	−2.79	−0.88	−0.18	−0.33
	10	3.145	2134.22	−221.7	−91.11	−42.1	−91.18
	20	3.533	3664.63	−294.83	−50.52	35.64	−97.1
	30	4.257	4539.68	−29.6	146.63	192.38	82.19
	38	5.551	4803.73	45.6	69.08	70.83	59.84

TABLE II. Mean absolute deviations in $\Delta U_j \equiv \overline{|U_j - U_{RKR}|}/D_e$; U_M, Morse; U_V, Varshni; U_L, Levine; U, this work. Parameter c is determined by minimizing the mean absolute deviation ΔU. E_{max} is the highest level in the data used.

Molecular state	ΔU_M (%)	ΔU_V (%)	ΔU_L (%)	ΔU (%)	c	t	ρ	x_0	E_{max}/D_e	Ref.
Li$_2$ $X\ ^1\Sigma_g^+$	8.36	6.63	7.70	2.14	−0.136 500	42.6527	355.126	−1.910 00	0.9998	9
Na$_2$ $X\ ^1\Sigma_g^+$	9.62	6.38	7.58	1.39	−0.205 716	62.7609	367.847	−4.771 72	0.9961	10
K$_2$ $X\ ^1\Sigma_g^+$	10.35	6.68	7.69	1.31	−0.266 348	75.8911	360.824	−10.8183	0.8306	11
Rb$_2$ $X\ ^1\Sigma_g^+$	12.26	7.84	8.87	1.52	−0.282 493	106.608	483.991	−14.6941	0.8388	12
Cs$_2$ $X\ ^1\Sigma_g^+$	16.12	10.30	11.44	1.20	−0.289 021	134.755	601.000	−18.0989	0.9944	8
Cl$_2$ $X\ ^1\Sigma_g^+$	6.06	1.08	1.11	1.89	−0.096 988	66.0428	746.980	−7.616 98	0.9995	13
Cl$_2$ $B\ ^3\Pi(O_u^+)$	5.30	2.30	2.51	1.30	−0.104 742	23.6854	249.817	−44.0794	0.9990	14
I$_2$ XO_g^+	8.03	2.70	1.58	1.38	−0.139 013	102.703	841.504	−39.2103	0.9997	15
ICl $X\ ^1\Sigma_g^+$	5.68	1.30	1.44	1.97	−0.086 212	84.1287	1059.96	−9.122 19	0.9970	16
ICl $A\ ^3\Pi_1$	8.42	3.96	2.35	0.76	−0.167 208	30.9785	216.249	−154.182	0.9934	17
ICl $A'\ ^3\Pi_2$	7.73	3.11	1.78	0.98	−0.157 361	37.5172	275.932	−87.8769	0.9853	18
HF $X\ ^1\Sigma^+$	4.48	3.14	3.00	1.96	0.127 772	27.3624	186.788	0.753 235	0.9928	19
H$_2$ $X\ ^1\Sigma_g^+$	5.76	7.53	4.48	2.65	0.170 066	20.9596	102.285	0.563 034	0.9922	20
CO $X\ ^1\Sigma^+$	0.87	3.05	2.27	0.36	0.044 624 6	87.3418	1869.91	0.532 232	0.6995	21
XeO $d\ ^1\Sigma^+$	6.78	5.13	6.18	3.69	−0.110 404	7.9588	80.0484	−641.956	0.9476	22
Average	7.72	4.74	4.67	1.63					0.9511	

first and second derivations at r_e, determined by experiments, but have different third and fourth derivations. The latter expressions in Eqs. (10) and (11) show the relation. The parameter c is adjustable and we choose it to minimize the absolute deviations. The results are given in Table II. We see that the mean absolute deviations of this potential are much less than that of the Morse potential for most states.

Another favorable character of this potential is the exact solvability. Firstly let us consider the Schrödinger equation for vibration of diatomic molecules with zero angular momentum

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + U(r) - E \right]\Psi = 0 \ . \tag{12}$$

Let

$$x = c \exp[-b(r-r_e)], \quad x_0 = c \exp(br_e) \ , \tag{13}$$

then the domain of r, $r \in [0, \infty)$ becomes

(i) $x \in (0, x_0]$ for $c > 0$;

(ii) $x \in [x_0, 0)$, for $c < 0$. $\qquad$ (14a)

From the calculation we know that $x_0 < 1$ if $c > 0$ and $x_0 \ll -1$ if $c < 0$ for most diatomic molecules. Since our potential fits the experimental curve closely, it is possible that our analysis is based on a real potential. For a real

diatomic molecule when $r \to 0$, the potential energy goes to infinity, and the wave function goes to zero. In a continuation, the wave function is zero also for $r < 0$. Therefore we have, in fact, a physical condition

$$\Psi = 0 \quad \text{for } r \in (-\infty, 0) \ . \tag{14b}$$

We now weakened the condition (14) to be

(i) $x \in [0,1]$, $\quad \Psi|_{x=0} = \Psi|_{x=1} = 0$ if $c > 0$ $\qquad$ (15a)

(ii) $x \in [-\infty, 0]$, $\quad \Psi|_{x=-\infty} = \Psi|_{x=0} = 0$ if $c < 0$. $\quad$ (15b)

One can check in the later Eq. (22) or (32) that the solution solved by the modified condition (15) is consistent with (14) in a high accuracy because of the quickly decreasing factor $(1-x)^{2\rho_c}$ with $2\rho \sim 10^3$ and $\rho_c = \text{sgn}(c)\rho$.

Using the variable x the Schrödinger equation (12) becomes

$$\left[\frac{d^2}{dx^2} + \frac{1}{x}\frac{d}{dx} - \frac{t^2(1-Qx)^2}{x^2(x-1)^2} + \frac{\lambda}{x^2} \right]\Psi = 0 \ , \tag{16}$$

with

$$t = (2\mu D_e)^{1/2}/(\hbar b), \quad Q = 1/c \ , \tag{17}$$

$$E = E_f\lambda, \quad E_f = \hbar^2 b^2/(2\mu) \ . \tag{18}$$

For the condition (15a) the general solution of Eq. (16) is

$$\Psi = x^{\rho_0}(1-x)^{(1/2)+\rho}[AF(\alpha,\beta,\gamma;x) + Bx^{-2\rho_0}F(\alpha-\gamma+1,\beta-\gamma+1,2-\gamma;x)] \ ,$$

where

$$\rho_0 = (t^2-\lambda)^{1/2}, \quad \rho = [\tfrac{1}{4}+t^2(Q-1)^2]^{1/2}, \quad \gamma = 1+2\rho_0, \quad \sigma = (t^2Q^2-\lambda)^{1/2} \ , \tag{19}$$

$$\alpha = \tfrac{1}{2}+\rho_0+\rho-\sigma, \quad \beta = \tfrac{1}{2}+\rho_0+\rho+\sigma \ , \tag{20}$$

and $F(\alpha,\beta,\gamma;x)$ is the hypergeometric function. $\Psi|_{x=0} = 0$ requires $B = 0$, then Ψ can be written as

$$\Psi = Ax^{\rho_0}(1-x)^{(1/2)+\rho}\left[\frac{\Gamma(\gamma)\Gamma(\gamma-\alpha-\beta)}{\Gamma(\gamma-\alpha)\Gamma(\gamma-\beta)}F(\alpha,\beta,\alpha+\beta-\gamma+1;1-x) \right.$$

$$\left. +(1-x)^{\gamma-\alpha-\beta}\frac{\Gamma(\gamma)\Gamma(\alpha+\beta-\gamma)}{\Gamma(\alpha)\Gamma(\beta)}F(\gamma-\alpha,\gamma-\beta,\gamma-\alpha-\beta+1;1-x) \right] \ .$$

For a real molecule $\alpha+\beta-\gamma = 2\rho \gg 1$. Hence $x \to 1$ leads to divergence of Ψ except for α or β being a negative integer. Letting $\alpha = -n$, we get the eigenvalue

$$\lambda_n = \tfrac{1}{2}t^2(Q^2+1) - \tfrac{1}{4}(\rho+\bar{n})^2 - \tfrac{1}{4}(\rho+\bar{n})^{-2}t^4(Q^2-1)^2$$

$$= (\rho+\bar{n})^{-2}[Qt^2(\bar{n}^2+\tfrac{1}{4}+2\bar{n}\rho) - \tfrac{1}{4}(\bar{n}^2+\tfrac{1}{4}+2\bar{n}\rho)^2] \ , \tag{21}$$

with

$$\bar{n} = n + \tfrac{1}{2} \ .$$

The latter expression of (21) is favorable in numerical computation for the cancellation of the large t^4 terms. The eigenfunction is

$$\Psi_n = N_n x^{\rho_{0n}}(1-x)^{(1/2)+\rho}F(-n,\beta_n,\gamma_n;x) \ , \tag{22}$$

where F becomes the Jacobi polynomial with energy-dependent indices; ρ_{0n}, β_n, and γ_n is expressed as in (19) and (20) with λ_n instead of λ. The normalization constant is calculated to be

$$N_n = \left[\frac{b}{n!} \frac{\Gamma(2\rho_{0n}+n+1)}{\Gamma(2\rho_{0n}+1)} \frac{\Gamma(2\rho+n+1+2\rho_{0n})}{\Gamma(2\rho+n+1)\Gamma(2\rho_{0n})} \frac{2\rho+2n+1+2\rho_{0n}}{2\rho+2n+1} \right]^{1/2} . \tag{23}$$

For the condition (15b) the general solution is

$$\Psi = x^{\rho_0}(1-x)^{(1/2)-\rho}[AF(\alpha',\beta',\gamma;x) + Bx^{-2\rho_0}F(\alpha'-\gamma+1,\beta'-\gamma+1,2-\gamma;x)] ,$$

with

$$\alpha' = \tfrac{1}{2}+\rho_0-\rho+\sigma, \quad \beta' = \tfrac{1}{2}+\rho_0-\rho-\sigma .$$

$\Psi|_{x=0}=0$ leads to $B=0$ again, then we see that $x \to -\infty$ makes $\Psi \to \infty$ except for α or β being negative integers. Letting $\alpha' = -n$, we obtain the eigenvalue expressed by (21) with the replacement of ρ by $-\rho$. The normalization constant is

$$N_n' = \left[\frac{e^{-i\pi 2\rho_{0n}}b}{n!} \frac{\Gamma(2\rho_{0n}+n+1)}{\Gamma(2\rho_{0n}+1)} \frac{\Gamma(2\rho-n)}{\Gamma(2\rho-n-2\rho_{0n})\Gamma(2\rho_{0n})} \frac{2\rho-2n-1-2\rho_{0n}}{2\rho-2n-1} \right]^{1/2} . \tag{24}$$

The eigenfunctions satisfy the orthonormalization

$$\int_D dx \frac{1}{b|x|} \Psi_m \Psi_n = \delta_{mn}, \quad D: \begin{cases} [0,1] & \text{if } c>0 \\ [-\infty,0] & \text{if } c<0 . \end{cases} \tag{25}$$

The wave functions may be used as a basis for large-amplitude vibration of molecules. Matrix elements of functions in this basis will be discussed elsewhere.[27]

III. SOLUTION FOR NONZERO ANGULAR MOMENTUM

The Schrödinger equation of vibration with nonzero total angular momentum J and neglected nuclear spin is

$$\left[-\frac{\hbar^2}{2\mu} \left[\frac{d^2}{d\tau^2} - \frac{L_J}{r^2} \right] + U(r) - E \right] \Psi = 0 , \tag{26}$$

where L_J is a given function of J. The equilibrium rotation constant is

$$B_e = \hbar^2/(2\mu r_e^2) .$$

Expanding r^{-2} as

$$r^{-2} = r_e^{-2}[1 - 2b^{-1}r_e^{-1}(1-Qx) + (3b^{-2}r_e^{-2} - b^{-1}r_e^{-1})(1-Qx)^2 + \cdots] \tag{27}$$

and neglecting the small terms $B_e L_J (1-Qx)^m$, $m \geq 3$, which contribute an energy of order $(\omega_e/D_e)^2 B_e L_J$ and $\omega_e^2 D_e^{-3}(B_e L_J)^2$, we get an effective potential

$$U_J = D_e(1-x)^{-2}(A_0 + A_1 x + A_2 x^2) , \tag{28}$$

with

TABLE III. Comparison of mean absolute deviations of large-domain potentials with that of small-domain potentials. $\Delta U_J \equiv |U_J - U_{RKR}|/D_e$; U_M, Morse; U_V, Varshni; U_L, Levine; U, this work.

Molecular state	n	ΔU_M (%)	ΔU_V (%)	ΔU_L (%)	ΔU (%)	c	E_{max}/D_e	Ref.
ICl $A'\,{}^3\Pi_2$	0–10	2.41	0.95	0.43	0.40	−0.168 583	0.4377	18
	0–20	5.33	1.99	0.88	0.75	−0.165 757	0.7516	
	0–30	7.08	2.71	1.57	0.79	−0.162 225	0.9311	
	0–38	7.73	3.11	1.78	0.98	−0.157 361	0.9853	
Cs$_2$ $X\,{}^1\Sigma_g^+$	0–40	4.46	2.91	3.21	0.42	−0.315 730	0.4274	8
	0–60	7.39	4.79	5.30	0.74	−0.307 473	0.6065	
	0–80	10.29	6.61	7.34	1.06	−0.300 856	0.7597	
	0–137	16.12	10.30	11.44	1.20	−0.289 021	0.9944	
CO $X\,{}^1\Sigma^+$	0–28	0.60	2.19	1.65	0.19	0.045 503 8	0.5670	23
	0–37	0.87	3.05	2.27	0.36	0.044 624 6	0.6995	21

TABLE IV. Experimental molecular constants used in this work.

State	r_e (Å)	D_e (cm^{-1})	ω_e (cm^{-1})	Ref.
Li$_2$ $X\,^1\Sigma_g^+$	2.673 24	8516.78	351.390	9
Na$_2$ $X\,^1\Sigma_g^+$	3.079 08	6022.6	159.177	24
K$_2$ $X\,^1\Sigma_g^+$	3.924 43	4440	92.3994	11
Rb$_2$ $X\,^1\Sigma_g^+$	4.2099	3950	57.7807	12
Cs$_2$ $X\,^1\Sigma_g^+$	4.648 00	3649.5	42.0203	8
Cl$_2$ $X\,^1\Sigma_g^+$	1.987 20	20 276.44	559.751	13
Cl$_2$ $B\,^3\Pi(O_u^+)$	2.4311	3341.17	255.38	14
I$_2$ XO_g^+	2.666 40	12 547.335	214.5208	25
ICl $X\,^1\Sigma^+$	2.320 91	17 557.6	384.27	17
ICl $A\,^3\Pi_1$	2.685	3814.7	211.0	17
ICl $A'\,^3\Pi_2$	2.665	4875.52	224.57	18
HF $X\,^1\Sigma^+$	0.916 81	49 384	4138.32	19
H$_2$ $X\,^1\Sigma_g^+$	0.741 599	38 297	4403.21	20
CO $X\,^1\Sigma^+$	1.128 32	90 529	2169.8136	26
XeO $d\,^1\Sigma^+$	2.852 30	693	156.832	22

$$A_0 = 1 + \frac{B_e L_J}{D_e}\left[1 + \frac{c^2 + 2c - 3}{br_e} + 3\frac{(1-c)^2}{b^2 r_e^2}\right],$$

$$A_1 = -Q\left[2 + \frac{B_e L_J}{D_e}\left(2c + 4\frac{c^2-1}{br_e} + 6\frac{(1-c)^2}{b^2 r_e^2}\right)\right], \tag{29}$$

$$A_2 = Q^2\left[1 + \frac{B_e L_J}{D_e}\left(c^2 + \frac{3c^2 - 2c - 1}{br_e} + 3\frac{(1-c)^2}{b^2 r_e^2}\right)\right].$$

A similar operation gives the J-dependent eigenvalue

$$E_{nJ} = E_f \lambda_{nJ},$$

$$\lambda_{nJ} = \tfrac{1}{2}t^2(A_0 + A_2) - \tfrac{1}{4}(\rho_{cJ} + \bar{n})^2 - \tfrac{1}{4}(\rho_{cJ} + \bar{n})^{-2}t^4(A_2 - A_0)^2, \tag{30}$$

with

$$\rho_{cJ} = \operatorname{sgn}(c)\rho_J, \quad \rho_J = [\tfrac{1}{4} + t^2(A_0 + A_1 + A_2)]^{1/2}. \tag{31}$$

The eigenfunction is

$$\Psi_{nJ} = N_{nJ}x^{\rho_{0nJ}}(1-x)^{(1/2)+\rho_{cJ}}F(-n,\beta_{nJ},\gamma_{nJ};x), \tag{32}$$

with

$$\rho_{0nJ} = (t^2 A_0 - \lambda_{nJ})^{1/2}, \quad \beta_{nJ} = 1 + n + 2\rho_{0nJ} + 2\rho_{cJ}, \quad \gamma_{nJ} = 1 + 2\rho_{0nJ}. \tag{33}$$

For the zero spin case we have $L_J = J(J+1)$. Writing E_{nJ} as the Dunham form

$$E_{nJ} = \sum_{m,l \geq 0} Y_{ml}(n + \tfrac{1}{2})^m J^l(J+1)^l, \tag{34}$$

we have the Dunham coefficients

$$Y_{00} = E_f \rho^{-2}(\tfrac{1}{4}Qt^2 - \tfrac{1}{64}) = \frac{\hbar^2 a^2}{2\mu}\left[\frac{c}{4} - \frac{t^{-2}c^2}{64}\left(\frac{1+c}{1-c}\right)^2 + O(t^{-4})\right],$$

$$Y_{10} = E_f[\tfrac{1}{2}\rho_c^{-3}t^4(Q^2-1)^2 - \tfrac{1}{2}\rho_c] = \hbar\omega_e\left[1 - t^{-2}\frac{c(1+c+c^2)}{8(1-c)^2} + O(t^{-4})\right],$$

$$Y_{20} = E_f[-\tfrac{1}{4} - \tfrac{3}{4}\rho^{-4}t^4(Q^2-1)^2] = \frac{\hbar^2 a^2}{2\mu}\left[-1 - c - c^2 + \tfrac{3}{8}t^{-2}c^2\left(\frac{1+c}{1-c}\right)^2 + O(t^{-4})\right], \tag{35}$$

$$Y_{30} = E_f \rho_c^{-5}t^4(Q^2-1)^2 = E_f t^{-1}\frac{c(1+c)^2}{(1-c)^3}\left[1 - \frac{5}{8}\frac{t^{-2}c^2}{(1-c)^2} + O(t^{-4})\right],$$

$$Y_{01} = B_e\left[1 - \frac{1}{4}t^{-2}\frac{c(1+c)}{(1-c)br_e} + O(t^{-4})\right].$$

IV. REMARKS

In Table I are listed the deviations from the RKR curves for five levels of three molecular states. The parameter c is determined by minimizing the mean absolute deviation of the four-parameter potential. We see that in the inner wall of the potential $(r < r_e)$ the deviations of the Morse potential become larger when the vibrational quantum number increases. This is true approximately for all of the 15 molecular states considered here. In the outer wall $(r > r_e)$ the deviations do not show the same trend. For most states here the above trend is preserved for the energy levels below $0.8D_e$, and the deviations go to zero when the energy levels go to D_e because of Eq. (1). For the $A'\,^3\Pi_2$ state of ICl as well as the ground states of HF and CO the deviations exhibit a minimum in the domain $r_e < r < \infty$. In any case the deviations of the four-parameter potential are less than that of the Morse potential except for a few levels, and the mean absolute deviations of the four-parameter potential are much less than that of the Morse potential, as shown in Table II. The improvement is most significant for the ground states of heavier alkali-metal dimers and I_2 as well as the $A\,^3\Pi_1$ and $A'\,^3\Pi_2$ states of ICl.

Tables I and III also present information on the comparison for the deviations of large- and small-amplitude vibrations. Although there is some complexity of the deviations in the outer wall of the potential, it is shown clearly in Table III that the mean absolute deviations of the Morse potential become larger for the vibrations of larger amplitudes (larger vibrational quantum numbers) and become very large for the potential domain extending to near the dissociation limit, while the mean absolute deviations of the four-parameter potential are still small.

For a list of experimental molecular constants used in this work please see Table IV.

In summary, the four-parameter potential may fit the experimental RKR curves more closely than the Morse potential; especially for large-amplitude vibrations its deviations are still much less than that of the Morse potential. Moreover, the corresponding Schrödinger equation can be solved exactly for $J = 0$ and be treated precisely for $J \neq 0$. The orthonormal eigenfunctions may be used as basis functions in the analytic evaluation of the large-amplitude bond-stretching vibrations and the couplings with other modes.

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