Phase shift differences for some exponential potentials

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Using the semi-empirical relations established by Tietz phase shift differences have been calculated for the Varshni and the Hulbert-Hirschfelder potential functions. From the expressions for the Hulburt-Hirschfelder potential those for the Morse have also been obtained. It has been observed that the two relations of Tietz lead to the same values for phase shift differences for all the potentials.

1. Introduction

In the last thirty years or so there has been a great development in many directions in the general theory of scattering, and the experimental studies in atomic and molecular collisions. In case of diatomic molecules the former may be considered a powerful tool for analysing the interactions between particles. For such analysis and for determining the corresponding phase shifts one requires to solve the Schrodinger equation with a potential energy function $V(r)$ representing the pair interactions between particles. However, the exact analytical solution of the said equation is too difficult to carry out in practice. In general, more accurate the potential, more complicated it is, and consequently more intractable the solution. Among the approximate methods one due to Tietz (1963) seems to be simple and straight forward, and for small values of l (l is the orbital angular momentum quantum number) is given by

$$\delta_l - \delta_{l+1} = \frac{\pi}{2k} \int_0^\infty r \frac{dU(r)}{dr} J_{1+1/2}(kr) J_{1+3/2}(kr) dr \qquad \ldots \quad (1)$$

$$\delta_{l-1} - \delta_{l+1} = \frac{(l+1/2)\pi}{k^2} \int_0^\infty \frac{dU(r)}{dr} J^2_{1+1/2}(kr) dr. \qquad \ldots \quad (2)$$

In an earlier study (De & Mohammad 1978) (hereafter referred to as I) we used these relations to determine the phase shift differences for some trigonometrical potentials $V(r)$. Our aim in the present investigation is to extend the study to some exponential functions of better performance.

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2. DERIVATION OF PHASE SHIFTS

A. *Varshni Potential*

In connection with discussions of the merits and demerits of various interaction potentials for the bound states of diatomic molecules, Varshni (1957) proposed seven empirical potential energy functions. Steele *et al* (1962) in their critical review and later Varshni & Shukla (1964) in a note have shown that the Varshni III potential

$$V(r) = D_e[(x-1)^2-1] \qquad \qquad \dots \ (3)$$

where

$$x = (r_e/r)\exp[-\beta(r^2-r_e^2)],$$
$$\beta = (\beta_1-1)/(2r_e^2), \qquad \beta_1 = (k_e r_e^2/2D_e)^{1/2}, \qquad \dots \ (4)$$

$-D_e$ is the minimum value of the potential, r_e is the value of r at which $V(r) = -D_e$ and k_e is the measure of the curvature at $r = r_e$, is a very good potential. Recently in a similar study (Mohammad 1978) it has been observed that this potential can fairly reproduce the RKR curves and can predict on the average, 3·46% deviation in the vibrational-rotational coupling constant α_e and 1·16% deviation in the vibrational anharmonicity constant $\omega_e x_e$ for the fifty different systems.

Substituting the value of $dU(r)/dr$ in eq. (1), we get after some manipulations

$$\delta_l-\delta_{l+1} = \frac{D_e\pi k^{2l+1}\alpha}{\Gamma\left(\frac{2l+3}{2}\right)\Gamma\left(\frac{2l+5}{2}\right)} \left[\frac{\Gamma(l+1)}{2^{2l+3}\beta^{l+1}} \left\{ F\left(l+2, l+1; \right.\right.\right.$$

$$\left.\frac{2l+5}{2}, 2l+3; -\xi_1\right) +2(l+1)F\left(l+2, l+2; \frac{2l+5}{2}, 2l+3; -\xi_1\right)\right\}$$

$$-\frac{\alpha\,\Gamma\left(\frac{2l+1}{2}\right)}{2^{3l+3\cdot5}\beta^{l+0\cdot5}} \left\{F\left(l+2, \frac{2l+1}{2}, \frac{2l+5}{2}, 2l+3; -\xi_2\right)\right.$$

$$\left.+\left(\frac{2l+1}{2}\right)F\left(l+2, \frac{2l+3}{2}, \frac{2l+5}{2}, 2l+3; -\xi_2\right)\right\} \right] \qquad \dots \ (5)$$

where

$$\alpha = r_e\exp(\beta r_e^2), \quad \xi_1 = k^2/\beta \text{ and } \xi_2 = \xi_1/2. \qquad \dots \ (6)$$

For the integration of eq. (1) to lead to eq. (5) the l values in the constituent terms have satisfied the condition $l > -1, -2, -1/2$ and $-3/2$ respectively. Since $-1/2$ is the lowest among these four terms, the lowest value that l in eq. (5) can have is zero.

In a similar manner we get

$$\delta_{l-1}-\delta_{l+1} = \frac{\pi D_e \alpha (2l+1)k^{2l-1}}{\left\{\Gamma\left(\frac{2l+3}{2}\right)\right\}^2}\left[\frac{\Gamma(l)}{2^{2l+2}\beta^l}\left\{F\left(l+1, l;\ \frac{2l+3}{2},\right.\right.\right.$$

$$\left. 2l+2;\ -\xi_1 \right)+2l\,F\left(l+1, l+1;\ \frac{2l+3}{2},\ 2l+2;\ -\xi_1\right)\right\}$$

$$-\frac{\alpha\,\Gamma\left(-\frac{2l-1}{2}\right)}{2^{3\,l+1\,5}\,\beta^{l-0\cdot5}}\left\{F\left(l+1,\ \frac{2l-1}{2}\ ;\ \frac{2l+3}{2},\ 2l+2;\ -\xi_2\right)\right.$$

$$\left.\left.+\left(\frac{2l-1}{2}\right)F\left(l+1,\ \frac{2l+1}{2};\ \frac{2l+3}{2},\ 2l+2;\ -\xi_2\right)\right\}\right] \qquad \dots (7)$$

For the integration of eq. (2) to lead to eq. (7) the l values in the constituent terms satisfy the condition $l > 0, -1, 1/2$, and $-1/2$ respectively. Thus the lowest l which eq. (7) can take is 1.

It is interesting to note that the sum of $\delta_0-\delta_1$ and $\delta_1-\delta_2$ as obtained from eq. (5) is exactly equal to $\delta_0-\delta_2$ obtained from eq. (7). Thus if δ_1 corresponding to a certain particular value of l (say l_0) is known any other phase shift δ_0, δ_1, δ_2, δ_3, ... can be very easily obtained from the above equations.

B. *Hulburt-Hirschfelder Potential*

Among the three parameter potential energy functions the one proposed by Morse (1929) has been most widely used. This is because it possesses a simple analytical form suitable for practical applications. However, this potential does not show a correct limiting behaviour at large internuclear distances. With a view to modifying it, Hulburt & Hirschfelder (1941) have added to it an expression which involves two more spectroscoipic constants, viz., α_e and $\omega_e x_e$. It is given by

$$V(r) = D_e[\exp(-2b(r-r_e))-2\exp(-b(r-r_e))]$$

$$+p(r-r_e)^3\exp(-2b(r-r_e))[1+q(r-r_e)] \qquad \dots (8)$$

where

$$b = (k_e/2D_e)^{1/2},\ p = b^3[1-(1+F)/br_e],$$

$$q = 2b-\frac{b^4}{p}\left[\frac{7}{12}-\frac{1}{b^2r_e^2}\left(\frac{5}{4}+\frac{5F}{2}+\frac{5F^2}{4}-\frac{G}{12}\right)\right],$$

$$F = \alpha_e\omega_e/6B_e^2\ \text{and}\ G = 8\omega_e x_e/B_e. \qquad \dots (9)$$

Here ω_e is the vibrational frequency and B_e is the equilibrium rotational constant. Steele et al (1962) in their critical review have observed that its average performance is the best of all potential functions for the bound states of diatomic molecules.

For this potential we substitute the value of $dU(r)/dr$ in eqs. (1) and (2), integrate the resulting integrals and get after some manipulations

$$\delta_l - \delta_{l+1} = \frac{D_e \pi k^{2l+1}}{2^{2l+3} \Gamma\left(\frac{2l+3}{2}\right) \Gamma\left(\frac{2l+5}{2}\right)} \left[\frac{a_1 \Gamma(2l+4)}{b^{2l+4}} F\left(l+2, l+2; 2l+3; -\zeta_1\right) \right.$$

$$+ \frac{1}{(2b)^{2l+8}} \left\{ a_2 \Gamma(2l+8) F\left(l+4, \frac{2l+9}{2}, l+2; \frac{2l+5}{2}, 2l+3; -\zeta_2\right) \right.$$

$$+ 2a_3 b \Gamma(2l+7) F\left(\frac{2l+7}{2}, l+4, l+2; \frac{2l+5}{2}, 2l+3; -\zeta_2\right)$$

$$+ 4a_4 b^2 \Gamma(2l+6) F\left(l+3, \frac{2l+7}{2}, l+2; \frac{2l+5}{2}, 2l+3; -\zeta_2\right)$$

$$+ 8a_5 b^3 \Gamma(2l+5) F(l+3, l+2; 2l+3; -\zeta_2)$$

$$\left. \left. + 16a_6 b^4 \Gamma(2l+4) F(l+2, l+2; 2l+3; -\zeta_2) \right\} \right] \qquad \cdots \quad (10)$$

and

$$\delta_{l-1} - \delta_{l+1} = \frac{\pi(2l+1)D_e k^{2l-1}}{2\left\{ \Gamma\left(\frac{2l+3}{2}\right) \right\}^2} \left[\frac{a_1 \Gamma(2l+2)}{2^{2l+1}b^{2l+2}} F(l+1, l+1; 2l+2; -\zeta_1) \right.$$

$$+ \frac{1}{2^{4l+7} b^{2l+6}} \left\{ a_2 \Gamma(2l+6) F\left(l+3, \frac{2l+7}{2}, l+1; \frac{2l+3}{2}, 2l+2; -\zeta_2\right) \right.$$

$$+ 2ba_3 \Gamma(2l+5) F\left(\frac{2l+5}{2}, l+3, l+1; \frac{2l+3}{2}; 2l+2, -\zeta_2\right)$$

$$+ 4b^2 a_4 \Gamma(2l+4) F\left(l+2, \frac{2l+5}{2}, l+1; \frac{2l+3}{2}, 2l+2; -\zeta_2\right)$$

$$+ 8b^3 a_5 \Gamma(2l+3) F(l+2, l+1; 2l+2; -\zeta_2)$$

$$\left. \left. + 16b^4 a_6 \Gamma(2l+2) F(l+1, l+1; 2l+2; -\zeta_2) \right\} \right] \qquad \cdots \quad (11)$$

where

$$\zeta_1 = 4k^2/b^2 \text{ and } \zeta_2 = \zeta_1/4,$$

$$a_1 = 2b \exp(br_e), \quad a_2 = -2pqb \exp(2br_e),$$

$$a_3 = [pq(4+2br_e-3r_e)-2pb]\exp(2br_e),$$

$$a_4 = [3p-12pqr_e(1+pr_e)+6p^2r_e]\exp(2br_e),$$

$$a_5 = [6pr_e^2(2q-b)+2pr_e(4bqr_e^2-3)]\exp(2br_e),$$

$$a_6 = 3pr_e^2+2(b-2)pqr_e^2-2b. \qquad \qquad \dots \quad (12)$$

It is interesting to note that the sum of $\delta_0-\delta_1$ and $\delta_1-\delta_2$ obtained from eq. (10) is exactly the same as $\delta_0-\delta_2$ from eq. (11). Thus eqs. (10) and (11) enable one to evaluate δ_0, δ_1, δ_2, δ_3 etc. very easily provided a certain particular δ_{l_0} is known.

The phase shift differences for the Morse potential will result if in the expressions for Hulburt-Hirschfelder potentials one puts $p - 0$. By this the phase shift differences for the Morse potential come out as

$$\delta_l-\delta_{l+1} = \frac{D_e \pi K^{2l+1} \Gamma(2l+3)}{2^{2l+5} \left\{ \Gamma\left(\frac{2l+3}{2}\right) \right\}^2 b^{2l+4}} \quad [8a_1 F(l+2, l+2; 2l+3; -\zeta_1)$$

$$-(b/2^{2l})F(l+2, l+2; 2l+3; -\zeta_2)] \qquad \dots \quad (13)$$

$$\delta_{l-1}-\delta_{l+1} = \frac{\pi(2l+1) \Gamma^{(l2+2)} D_e R^{2l-1}}{\left\{ \Gamma\left(\frac{2l+3}{2}\right) \right\}^2 b^{2l+2}2^{2l+3}} \quad [2a_1 F(l+1, l+1; 2l+2; -\zeta_1)$$

$$-(b/2^{2l})F(l+1, l+1; 2l+3; -\zeta_2)]. \qquad \dots \quad (14)$$

3. Discussion

From the above study it is seen that the Tietz formula is most suitable for analytical determination of phase shifts provided an accurate interaction potential $V(r)$ as well as an individual phase shift δ_{l_0} is known.

As according to almost all accurate methods the value of δ_l very rapidly decreases as l is increased, the numerical value of $\delta_l = \delta_{l_0}$ for a certain larger value l_0 obtained from all these methods are unlikely to differ much in magnitude. The most simple relation to determine δ_l is that due to Born (see Davydov 1965) and we think that the Born value of δ_{l_0} for the said particular value of l_0 can be safely considered to be equal to that due to Tietz. We can expect that with the knowledge of this Born value of δ_{10}, the quantities δ_{l_0-1}, δ_{l_0-2}, ... δ_0 etc. obtained from relations (5), (7), (11) and (11) for the two potentials would be reasonly accurate.

REFERENCES

Davydov A. S. 1965 *Quantum Mechanics*, Pergamon Press Inc., New York, p. 467.

De S. K. & Noor Mohammad S. 1978 *Ind. J. Phys.* (to be published).

Gradshteyn I. S. & Ryzhik I. M. 1965 *Table of Integrals Series and Products*, Academic Press, New York.

Hulburt H. M. & Hirschfelder J. O. 1941 *J. Chem. Phys.* **9**, 61.

Luke Y. L. 1962 *Integrals of Bessel functions*, McGraw Hill Book Co. Inc., New York, p. 312.

Morse P. M. 1929 *Phys. Rev.* **34**, 57.

Noor Mohammad S. 1978 *Physica (to be published)*.

Steele D., Lippincott E. R. & Vanderslice J. T. 1962 *Rev. Mod. Phys.* **34**, 239.

Tietz T. 1963 *Acta Phys. Hung.* **16**, 289.

Varshni Y. P. 1957 *Rev. Mod. Phys.* **29**, 664.

Varshni Y. P. & Shukly R. C. 1964 *J. Chem. Phys.* **40**, 250.