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J. F. Ogilvie

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J. F. Ogilvie
Guelph-Waterloo Center for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada and Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan

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The conditions applicable at the limits of the united atom and the separate atoms may be applied to any radial function for diatomic molecules based on the argument $z \equiv 2(R - R_e)/(R + R_e)$ so as to generate further coefficients in a polynomial representation that thus has the correct asymptotic behavior in the approach to these limits. The appropriate conditions are given for the potential-energy and dipole-moment functions, and the results are illustrated by application to HCl. This type of representation is compared with rational functions.

I. INTRODUCTION

Several years ago there was introduced[1] a general internuclear potential-energy function for diatomic molecules that was both flexible enough to be as accurate as desired and lacking in any problem due to a finite range of the radius of convergence based on the equilibrium internuclear separation R_e as the expansion center. Of course such a function is based on the approximation of separate treatment of the electronic and nuclear motions. The argument $z \equiv 2(R - R_e)/(R + R_e)$ of this function is a member of a family[1] of arguments $w_{mn} = (m+n)(R - R_e)/(mR + nR_e)$, but only it treats the two limits, the united atom at $R = 0$ and the separate atoms as $R \rightarrow \infty$, on an equivalent basis, specifically $z = -2$ and $+2$, respectively. The potential-energy function $V(z)$ based on this argument has the form of a polynomial, to be truncated as necessitated either by a particular range of R of interest or by limited data to define this function. This form is similar to the potential-energy function $V(x)$, $x \equiv (R - R_e)/R_e$, due to Dunham[2] (following Kratzer[3]); in fact the former, $V(z)$, may be transformed to the latter, $V(x)$, through the substitution

$$z = \frac{2x}{2+x} \approx x\left(1 - \frac{x}{2} + \frac{x^2}{4} - \frac{x^3}{8} + \cdots\right).$$

This substitution can also serve to furnish the relationships between the coefficients c_j in $V(z)$,

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{J} c_j z^j\right)$$

and a_j in $V(x)$,

$$V(x) = a_0 x^2 \left(1 + \sum_{j=1}^{J} a_j x^j\right)$$

as given[1] previously. It should be stressed that the expansion $V(x)$, and hence its expansion coefficients, are meaningful only when $|x| < 1$.

Some relations have also been given[1] for the purpose of generating further coefficients c_j, beyond those determined, for instance, from spectroscopic data through the known dependence[4] of the vibration–rotational term coefficients Y_{kl} on these c_j and R_e, from the knowledge of the limiting behavior of $V(z)$ at large distances, $R \gg R_e$. Thus the applicable condition is that

$$[(R^2 d/dR)^p V(r)] \rightarrow 0 \quad \text{as } R \rightarrow \infty$$

for values of the exponent $p < n$, n being the exponent in the leading term of the asymptotic expansion[5] of $V(R)$ at large R, namely

$$V(r) = \mathscr{D}_e - \sum_{m > n} C_m R^{-m}.$$

This expansion is valid in the absence of effects of both electronic degeneracy and fine structure, and in the case that there is negligible distortion, due to interatomic interactions, of the distribution of electronic density relative to the separate atoms.

In this report we extend these relations to take into account the applicability of any known, nonzero values of the coefficients C_m and illustrate their application to the molecule HCl. We also present a dipole-moment function as a polynomial likewise based on the argument z, and show the corresponding relations for the limiting behavior of this function in the asymptotic approach to both limits $z = \pm 2$. In both these cases of potential-energy and dipole-moment functions, and by analogy any other function of internuclear separation also based on this argument z, we demonstrate that this choice of argument in a truncated power series can be a useful alternative to rational functions for the accurate, economical, and convenient representation of radial properties of diatomic molecules.

II. POTENTIAL-ENERGY FUNCTION

By using the defining relation

$$C_m \equiv \{(-R^2 d/dR)^m [\mathscr{D}_e - V(z)]\}/m! \|_{R \rightarrow \infty}$$

one can obtain the set of equations

$$C_m = (-1)^{m+1} c_0 R_e^m \Big[2^4 m + \sum_{j=1}^{n'} 2^{j+m+2} \times (j+2) c_j p_m(j)/m! \Big]$$

in which $p_m(j)$ is a polynomial given in Table I. In this equation the summation is over all the n' values of the coefficients c_j ($0 \leqslant j \leqslant m'$) typically determined from spectroscopic data and the $m'' = n' - m'$ values of further coefficients c_j treated as unknown quantities; the latter are then determined according to the solution of the m'' simultaneous linear equations with the known values of C_m. Furthermore, the finite value of $V(z)$, namely the equilibrium binding en-

TABLE I. Polynomials $p_m(j)$ in the expressions for the coefficients C_m in the potential-energy function at large R.

$$p_1(j) = 1$$

$$p_2(j) = j + 2$$

$$p_3(j) = j^2 + 4j + \tfrac{9}{2}$$

$$p_4(j) = (j+2)(j^2 + 4j + 6)$$

$$p_5(j) = j^4 + 8j^3 + 29j^2 + 52j + \tfrac{75}{2}$$

$$p_6(j) = (j+2)(j^4 + 8j^3 + 34j^2 + 72j + \tfrac{135}{2})$$

$$p_7(j) = j^6 + 12j^5 + 155j^4/2 + 300j^3 + 709j^2 + 948j + \tfrac{2205}{4}$$

$$p_8(j) = (j+2)(j^2 + 4j + 10)(j^4 + 8j^3 + 46j^2 + 120j + 126)$$

$$p_9(j) = j^8 + 16j^7 + 154j^6 + 952j^5 + 4039j^4 + 11704j^3 + 22266j^2 + 25128j + \tfrac{25\,515}{2}$$

$$p_{10}(j) = (j+2)(j^8 + 16j^7 + 172j^6 + 1168j^5 + 5623j^4 + 18616j^3 + 41454j^2 + 55800j + \tfrac{70\,875}{2})$$

$$p_{11}(j) = j^{10} + 20j^9 + 525j^8/2 + 2280j^7 + 14448j^6 + 67200j^5 + 458575j^4/2 + 559420j^3 + 1850877j^2/2 + 930330j + \tfrac{1\,715\,175}{4}$$

ergy $\mathscr{D}_e$, as $R \to \infty$ or $z = 2$, implies the further condition

$$\mathscr{D}_e = 4c_0\left(1 + \sum_{j=1}^{n'} 2^j c_j\right);$$

use of this additional condition requires that m'' be increased by unity. The function $V(z)$ is well behaved at the limit of the united atom, $R = 0$ or $z = -2$; using the condition that $V(R) \to \infty$ as $R \to 0$, because of the Coulombic repulsion between the nuclei, one can derive another equation

$$1 + \sum_{m=1}^{n'+1} \left\{ m!^{-1} \left[\sum_{j=1}^{n'+1} (-1)^j 2^j c_j \right]^m \prod_{k=0}^{j-1} (-k-1) \right\} = 0\,.$$

Because of the nonlinear combination of the coefficients c_j, this relation is less likely to be useful than those given above.

III. DIPOLE-MOMENT FUNCTION

The polynomial function to represent the radial dependence of the electric dipole moment of a diatomic molecule is expressed in terms of z as

$$M(z) = \sum_{j=0}^{J} P_j z^j$$

by analogy with the function due to Dunham[6]:

$$M(x) = \sum_{j=0}^{J} M_j x^j\,.$$

Then the relations to interconvert the coefficients P_j and M_j are

$$M_0 = P_0\,,$$

$$M_k = \sum_{j=1}^{k} (-1)^{k-j}(k-1)!\,2^{j-k}P_j/[(k-j)!(j-1)!]\,,$$

and

$$P_k = \sum_{j=1}^{k} (k-1)!\,2^{j-k}M_j/[(k-j)!(j-1)!], \quad k > 0\,.$$

This function $M(z)$ is potentially useful to represent the dipole moment because certain limiting conditions can be applied to $M(z)$ through sums of the coefficients P_j, entirely analogous to those above for the potential-energy function. For a neutral diatomic molecule that dissociates into neutral atoms, the common behavior of ground electronic states of neutral molecules, these conditions[7] are: (i) $M(R) = 0$ at $R = 0$ and $R \to \infty$; (ii) $M(R) \to 0$ according to R^{-n} as $R \to \infty$, the value of n depending on the angular momenta of the states of the separate atoms[8]; (iii) $M(R) \to 0$ according to R^m as $R \to 0$, the value depending on the angular momentum of the state of the united atom.[8]

According to the second criterion, the following conditions are obtained for the coefficients C_k in the expansion

$$M(R) = \sum_{k=0} C_k R^{-k}\,,$$

$$C_0 = \sum_{j=0} 2^j P_j \quad (=0)\,,$$

$$C_1 = \sum_{j=1} -2^{j+1} j P_j R_e\,,$$

$$C_2 = \sum_{j=1} 2^{j+2} j^2 P_j R_e^2/2!\,,$$

$$C_3 = \sum_{j=1} -2^{j+3} j(j^2 + \tfrac{1}{2}) P_j R_e^3/3!\,,$$

$$C_4 = \sum_{j=1} 2^{j+4} j^2(j^2 + 2) P_j R_e^4/4!\,,$$

$$C_5 = \sum_{j=1} -2^{j+5} j(j^4 + 5j^2 + \tfrac{3}{2}) P_j R_e^5/5!\,,$$

$$C_6 = \sum_{j=1} 2^{j+6} j^2(j^4 + 10j^2 + \tfrac{23}{2}) P_j R_e^6/6!\,,$$

$$C_7 = \sum_{j=1} -2^{j+7} j(j^6 + 35j^4/2 + 49j^2 + \tfrac{45}{4}) P_j R_e^7/7!\,.$$

Similarly, according to the third criterion, the following conditions are obtained for the coefficients C'_k in the expansion

$$M(R) = \sum_{k=0} C'_k R^k\,,$$

$$C'_0 = \sum_{j=0} (-2)^j P_j \quad (=0)\,,$$

$$C'_1 = \sum_{j=1} (-2)^{j+1} j P_j/R_e\,,$$

$$C'_2 = \sum_{j=1} (-2)^{j+2} j^2 P_j/(2!R_e^2)\,,$$

$$C'_3 = \sum_{j=1} (-2)^{j+3} j(j^2 + \tfrac{1}{2}) P_j/(3!R_e^3)\,,$$

$$C'_4 = \sum_{j=1} (-2)^{j+4} j^2(j^2 + 2) P_j/(4!R_e^4)\,,$$

$$C'_5 = \sum_{j=1} (-2)^{j+5} j(j^4 + 5j^2 + \tfrac{3}{2}) P_j/(5!R_e^5)\,.$$

In these equations for C_k and C'_k, the summations are over the $n' = n'' + m' + m'' + 3$ coefficients P_j of which those numbering $n'' + 1$ with $0 \leqslant j \leqslant n''$, typically determined from the Stark effect in microwave spectra (P_0) and from the intensities of infrared vibration-rotational transitions (P_j, $1 \leqslant j \leqslant n''$), are treated as known parameters in the set of $m' + m'' + 2$ simultaneous linear equations employing $m'' + 1$ coefficients C_k, $0 \leqslant k \leqslant m''$, and $m' + 1$ coefficients C'_k, $0 \leqslant k \leqslant m'$. Generally the nonzero values of the coefficients C_k and C'_k may be unknown; in that case only the zero values would be used. The number of these zero values depends on the angular momenta of the states of the united and separate atoms, specifically for a neutral diatomic molecule that dissociates into neutral atoms as follows.[8] If the atomic dissociation products each have total (electronic) angular momentum of magnitude less than $\hbar$, then the leading term in the expansion of $M(z)$ as $R \to \infty$ is proportional to R^{-7}; in all other cases, the corresponding dependence is R^{-4}. As $R \to 0$, there is a dependence on R^3 for the united atom in an S or P state, but on R^5 for a D or F state.

If the diatomic molecule carries a single net electrical charge, then the dependence on R in the limit of the united atom remains the same. At relatively large distances, $R \gg R_e$, however, the dipole moment increases linearly with distance instead of decreasing to zero. The approach to this linear dependence is according to a dependence on R^{-2}. For multiply charged diatomic ions, the appropriate limiting dependences can be easily determined. In all these cases, which coefficients C_k have zero values can be easily deduced, so the appropriate equations above can be selected.

IV. APPLICATION TO THE POTENTIAL-ENERGY FUNCTION OF HCl

The potential-energy function of the ground electronic state of HCl is well determined from spectroscopic data, up to at least half the dissociation limit.[9] From these results the coefficients c_j, $0 \leqslant j \leqslant 8$, of the function $V(z)$ are calculable, and are listed in Table II. By means of various combinations of these c_j and the relations given above, one can test the applicability of the theory to HCl. Because the dissociation products of the ground electronic state of HCl are H ^{2}S and Cl ^{2}P atoms, the value of the exponent of the leading term in the long-range expansion of the potential energy is $n = 6$; thus $C_k = 0$, $1 \leqslant k \leqslant 5$. The equilibrium binding energy $\mathscr{D}_e$ can be estimated from thermodynamic data,[10], more accurately than from present spectroscopic data, but including the zero-point energy from spectroscopic data,[9] to be (in wave number units) $(3.7252 \pm 0.0011) \times 10^6$ m^{-1}. Although some semiquantitative values of C_6 and C_8 have been published,[11] in the results given here the values of C_6, C_8, and C_{10}, also listed in Table II, were estimated from other experimental and theoretical data; tests with the other values[11] (although lacking C_{10}) showed that the results were insensitive to the values of these parameters within moderate ranges of variation.

In Fig. 1 are plotted the potential-energy functions $V(z)$ for three different cases of choices of the coefficients c_j. One curve simply uses the set c_j, $0 \leqslant j \leqslant 8$, determined from the spectra of various isotopic species in the range of energy up to $0.52\,\mathscr{D}_e$. Another curve is based on c_0, c_1 and c_2 from the spectra and then a further nine c_j generated from the use of $\mathscr{D}_e$ and C_k, $1 \leqslant k \leqslant 8$; a related function from the use of C_9 in addition produces a curve indistinguishable from this one. The third curve uses c_j, $0 \leqslant j \leqslant 4$, from the spectroscopic data and 12 further long-range conditions, specifically $\mathscr{D}_e$ and C_k, $1 \leqslant k \leqslant 11$. The values of the potential-energy coefficients c_j of the functions corresponding to the illustrated curves are listed in Table III. For purposes of comparison, another set of coefficients c_j also appears in Table III; these coefficients are determined from c_0, $\mathscr{D}_e$ and only the near-dissociation conditions C_k, $1 \leqslant k \leqslant 11$, but the curve would show a maxi-

TABLE II. Values of the potential-energy coefficients c_j and C_j used in generating the extended potential-energy functions, with the values of the coefficients in Table III and the curves in Fig. 1.

$c_0 = 2.111\,393 \times 10^7$ m^{-1}
$c_1 = -1.363\,372\,5$
$c_2 = 0.865\,517$
$c_3 = -0.473\,118$
$c_4 = 0.089\,594$
$c_5 = 0.156\,448$
$c_6 = -0.606\,10$
$c_7 = -0.375\,05$
$c_8 = 1.260\,1$
$\mathscr{D}_e = 3.7252 \times 10^6$ m^{-1}
$C_6 = 1.2 \times 10^{-53}$ m^5
$C_8 = 1.2 \times 10^{-73}$ m^7
$C_{10} = 1.2 \times 10^{-93}$ m^9
$C_k = 0, 1 \leqslant k \leqslant 5$
$C_7 = C_9 = C_{11} = 0$

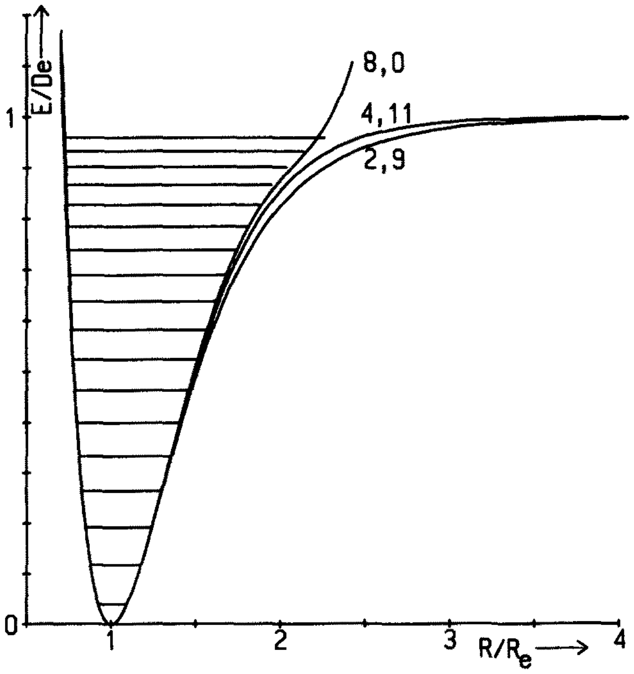

FIG. 1. Potential-energy curves and vibrational amplitudes of HCl; the digits beside each curve where they are distinct indicate the values of m' and m'', respectively.

TABLE III. Values of the coefficients c_j used in generating the potential-energy functions shown in Fig. 1, with another set for an R^{-6} attraction for comparison.

j	$m' = 2,\ m'' = 9$	$m' = 4,\ m'' = 11$	$m' = 0,\ m'' = 11$
0	$2.111\,393 \times 10^7\ \mathrm{m}^{-1}$	$2.111\,393 \times 10^7\ \mathrm{m}^{-1}$	$2.111\,393 \times 10^7\ \mathrm{m}^{-1}$
1	− 1.363 372 5	− 1.363 372 5	− 4.526 8
2	0.865 517	0.865 517	10.119 4
3	− 2.088 83	− 0.473 118	− 14.119 3
4	5.121 56	0.089 594	13.424 9
5	− 6.569 50	− 7.059 48	− 9.056 14
6	5.031 00	33.079 9	4.402 15
7	− 2.476 19	− 69.804 7	− 1.537 75
8	0.797 60	89.025 6	0.377 65
9	− 0.163 59	− 76.527 3	− 0.062 07
10	0.019 48	46.566 1	0.006 13
11	− 0.001 03	− 20.451 1	− 0.000 28
12		6.476 2	
13		− 1.447 7	
14		0.217 4	
15		− 0.019 7	
16		0.000 82	

mum in the potential energy about 40% above the dissociation limit near $R \sim 2R_e$. The classical vibrational amplitudes of $^1H^{35}Cl$ determined[12] by means of the RKR procedure are also plotted on this figure; the differences between the points at the ends of these lines pertaining to a specific isotopic species and the corresponding mass-independent potential energy represented by the curves are negligible on the scale of this figure. Some other combinations of some ($\leqslant 9$) c_j from the spectroscopic data and some (between 1 and 12) long-range conditions (always including $\mathscr{D}_e$) produced a local maximum in the generated curve in the region $3.5 \leqslant R/R_e \leqslant 9$, followed by a shallow minimum before the proper asymptotic approach to the dissociation limit. In some cases, an absolute maximum appeared in the curve in the region $R < 0.5R_e$; the curve diverged negatively as $R \to 0$.

V. DISCUSSION

A comparison of two curves in Fig. 1, specifically the curve for the function from spectroscopic data alone and either other curve embodying some long-range conditions indicates the practical utility of the combination of the use of the argument z in the potential-energy function and the long-range conditions. On the other hand, the comparison between either curve using the long-range conditions and the classical amplitudes demonstrates what is in any case intuitively obvious, namely that, even with certain long-range conditions applied, the functions cannot be quantitatively accurate in the region intermediate between the region near R_e defined by the spectroscopic data and the really long-range region (in which, ironically, retarded dispersion forces prevail such that the conventional near-dissociation approach[5] requires modification). Nevertheless the latter functions are qualitatively accurate, and with the imposition of further information could presumably be made more accurate. The long-range conditions incidentally bestow good behavior on the short-range portion of the curves; in most cases, in which there is no maximum of the curve in the region $0 < R < R_e$, fortuitously the energy reached at $R \approx 0$ is approximately what is expected, $\sim 2 \times 10^{12}\ \mathrm{m}^{-1}$, on the basis of just the Coulombic repulsion between the nuclei (at the maximum before nuclear fusion), although generally the initial approach ($R < R_e$) to this point is steeper than what the RKR turning points indicate. Thus in these cases, the potential-energy function generated by means of some combination of the spectroscopic data and the long-range conditions is able to provide a qualitatively correct behavior throughout the entire range of internuclear separation, and of course also quantitatively correct in some region about R_e according to the spectroscopic data embodied therein.

It is worthwhile to compare the qualities of these polynomials in the argument z, truncated but including the effects arising from the application of long-range and short-range conditions, and rational functions such as Padé approximants. The disadvantages of each representation are fairly obvious even from its form. The polynomial can be of a large order. For instance, the application of 12 long-range conditions to extend the nine spectroscopically determined coefficients c_j generates a polynomial of order 20; in the case of the dipole-moment function, the application of only four long-range conditions and three short-range conditions, in both cases just the number of conditions (for HCl, for instance) with C_k and C'_k having zero values, produces an extra seven terms to be added to the eight ($P_0 - P_7$) coefficients determined spectroscopically so as to generate a polynomial of order 14. Even within the range $-2 \leqslant z \leqslant 2$, such polynomials may in general be expected to have unwanted maxima or minima. In contrast, although a rational function may be formulated to have the proper long-range and short-range behaviors, additional unwanted maxima and minima may also occur; moreover, a pole in the polynomial in the denominator can give catastrophic behavior, even within a region of interest. A Padé function might in some cases be formulated to yield the correct asymptotic behaviors without permitting a sufficiently large number of parameters to be quantitatively accurate within a particular region of interest; however the analogous situation cannot in principle arise with the truncated polynomial representations.

Beside the potential-energy and dipole-moment functions that have been particularly discussed in this paper, an analogous treatment can obviously be applied to any other radial function of a diatomic molecule. Specifically, a function to represent a quantity for, or component of, electric polarizability and hyperpolarizability that governs the intensity of transitions in Raman and hyper-Raman scattering spectroscopy, the spin–orbit function $A(z)$ of molecules in Π electronic states, the electric quadrupole function $Q(z)$ of molecules having nuclei with spin$\geqslant\hbar$, and functions expressing the radial dependence of adiabatic and nonadiabatic corrections may all be amenable to this approach. The potential-energy function might also be extended to apply to various coordinates of polyatomic molecules, as the correct asymptotic behavior is likely to produce more accurate results in molecular dynamics calculations than the extended Rydberg function[13] with its exponential approach to the dissociation limit.

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