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A general potential energy function for diatomic molecules

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A new and flexible function that is a valid representation of the potential energy of diatomic molecules within the entire range of accessible internuclear separations is proposed. This function is shown to be a member of a family of functions that includes previous polynomial functions having more restricted validity. Methods of generating the coefficients (parameters) of the new function are described, and tables of these parameters for a selection of molecules, including some ground and some excited electronic states, are presented.

INTRODUCTION

The structure of a free diatomic molecule is described incompletely by only its equilibrium internuclear separation. Because local maxima of electron density in molecules coincide with nuclear positions, the concept of molecular structure – such as is incorporated in a bond length – remains valid even without the formal assumption of separation of nuclear and electronic motions, at least for the ground electronic state. But this Born–Oppenheimer (1927) procedure makes possible the definition of a potential energy function, describing how the electronic energy plus nuclear repulsion depends upon the internuclear distance. Such a function embodies a full description of the molecular structure, by definition for a given electronic state but independent of vibrational and rotational quantum numbers, under conditions in which the Born–Oppenheimer approximation is applicable, namely absence of curve crossings which cause failure of the molecule to be characterized according to a single electronic state (Wilson 1979).

The analytic representation of these potential energy functions is an enduring problem. Although the harmonic oscillator model has long been popular as a limiting case of diatomic vibrational motion, it is a poor approximation for any real molecule. More realistic (but still simple) functions have been devised by Lennard-Jones (1924) and Morse (1929); although these functions display the requisite qualities of a finite dissociation energy, relative to the energy minimum corresponding to molecular existence, and a rapid increase of energy at distances less than that of this subsidiary minimum, no real molecule adheres faithfully to either energy function. On the other hand, the series function devised by Dunham (1932) has a flexible form and can represent the potential energy near the equilibrium separation within the accuracy of the Born–Oppenheimer approximation, but fundamentally lacks convergence at larger distances. Many other potential energy functions have been proposed, none entirely successful (Goodisman 1973).

A typical potential energy function is depicted qualitatively in figure 1; here the entire régime from united atom to separated atoms is shown for carbon(II) oxide. The absolute minimum of energy occurs about 10^{-15} m for the united atom silicon, in comparison with which the secondary minimum about 10^{-10} m seems negligible. Because of the intervening large maximum of energy, corresponding to internuclear repulsion, the secondary minimum is however significant and thereby accounts for molecular stability, the discrete existence of a durable molecular species. This diagram also demonstrates the full range of behaviour that an analytic potential energy function should ideally encompass. In practice the region less than 10^{-12} m may be ignored both because of lack of experimental information by which such a function might be defined, and because in molecular science the regions near the secondary minimum are much more pertinent. This diagram also serves to define, besides the position of relative zero of the energy ordinate, the 'well' depth $\mathscr{D}_e$ and the equilibrium internuclear separation R_e, the primary indices of a diatomic molecular structure.

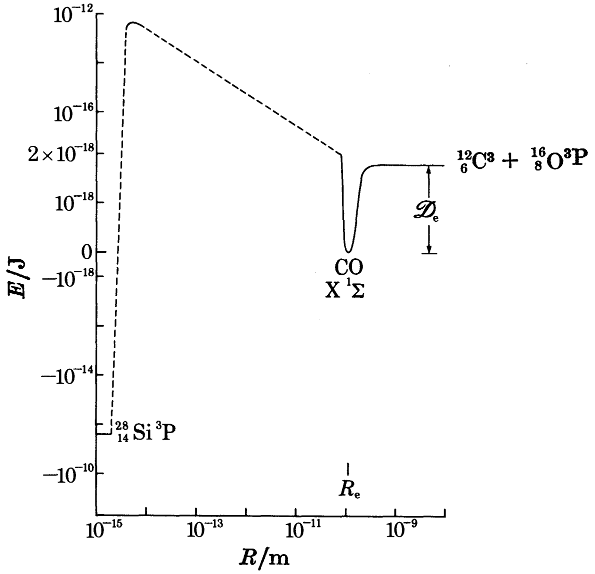

FIGURE 1. Qualitative representation of potential energy of carbon(II) oxide throughout the range of separations from united atom (silicon) to separated atoms. Note that the ordinate scale is discontinuous.

In this article a further potential energy function is presented that is in principle capable of faithfully representing the variation of energy, within the Born–Oppenheimer approximation, with distance at all separations greater than that of the region of the internuclear repulsion maximum. The relation of the new function to previously existing forms will be discussed, and its application to various molecules will be demonstrated.

FORM OF REPRESENTATION

We can consider the general form of the potential energy of a diatomic molecule as a function of some general parameter related to instantaneous internuclear separation R to be represented as a truncated polynomial or power series of argument w as follows:

$$U(w) = d_0 w^2 \left(1 + \sum_{i=1}^{k} d_i w^i\right).$$

Then the Dunham (1932) form of function is obtained by taking

$$w \rightarrow x \equiv (R - R_e)/R_e,$$

in which case the coefficients d_i, $0 \leqslant i \leqslant k$, are written as a_i. Another form of function was devised by Simons *et al.* (1973) with

$$w \rightarrow y \equiv (R - R_e)/R$$

and coefficients here written as b_i. A further form is here presented as

$$w \rightarrow z \equiv (R - R_e)/\tfrac{1}{2}(R + R_e),$$

with the coefficients d_i written as c_i. With this definition of z, each representation has the same harmonic oscillator limit at R infinitesimally different from R_e; i.e. for $R \sim R_e$, $x \sim y \sim z$ and $a_0 \equiv b_0 \equiv c_0$. In each case the series expansion is made about $R = R_e$. Thus $z = 2x/(2+x) = 2y/(2-y)$.

The values of the arguments w can be compared at various separations:

w	$R = 0$	$R = 0.5R_e$	$R = R_e$	$R = 2R_e$	$R \rightarrow \infty$
x	-1	-0.5	0	1	$\rightarrow \infty$
y	$\rightarrow -\infty$	-1	0	0.5	$\rightarrow 1$
z	-2	-0.67	0	0.67	$\rightarrow 2$

Thus of these three arguments, only z remains finite at all separations. Furthermore the vibrational potential has effectively a pole at internuclear separation corresponding to the united atom limit, $R = 0$; this pole limits the domain of convergence according to the $U(x)$ function within the range $|x| < 1$, or $0 < R < 2R_e$, because the point $R = R_e$ has been taken as the expansion centre (Beckel 1976). A singularity in $U(y)$ as $R \rightarrow \infty$ would also limit this $U(y)$ function to a range of validity $|y| < 1$, or $0.5R_e < R < \infty$. Thus the $U(x)$ function is practically useful only near the minimum of the internuclear potential corresponding to molecular stability, whereas the $U(y)$ function fails to be usable at the smaller separations corresponding to distances attainable in, for instance, scattering experiments with relatively energetic ($U \gg \mathscr{D}_e$) translational motion. On the other hand, the $U(z)$

function treats equivalently the limiting cases of united atom and separated atoms, i.e. $z = \pm 2$, but there is no multivaluedness introduced. Thus of these three series representations, only the $U(z)$ function is valid throughout the entire range of internuclear separations pertinent to interatomic interactions.

The substitution $\rho \equiv \frac{1}{2}(R+R_e)$ converts z into

$$z \equiv (R-R_e)/\tfrac{1}{2}(R+R_e) \rightarrow \rho - R_e/\tfrac{1}{2}\rho,$$

which is equivalent to the expansion variable of the $U(y)$ function. Therefore the quantum-mechanical basis for the $U(z)$ expansion is similarly established (Simons *et al.* 1973; Thakkar 1975). It is planned to present wave functions and matrix elements based on the $U(z)$ potential in a separate article.

DETERMINATION OF COEFFICIENTS c_i

For the two model potentials, of exponential or inverse-power types, the coefficients of powers of z in $U(z)$ can be expressed analytically. For the potential function due to Morse (1929), which may be expressed in terms of R as

$$U(R) = \mathscr{D}_e(1-e^{-a(R-R_e)})^2, \quad a > 0,$$

the coefficients are

$$c_0 = \mathscr{D}_e(aR_e)^2,$$

$$c_k = 2^{-k}(k+1) + \sum_{j=0}^{k-1} \frac{(k+1)!\,(2^{k-2j+2} - 2^{1-j})\,(-aR_e)^{k-j}}{j!(k+1-j)!\,(k+2-j)!}, \quad k > 0.$$

This series converges relatively rapidly, although not monotonically in magnitude of c_i. For instance for $aR_e = 3$, $a_{12} = 0.0999$, $b_{12} = 0.232$ and $c_{12} = 0.000\,306$; these values indicate the relative convergence rates for the three series for this potential function, which is qualitatively realistic.

Another model potential may be written

$$U(R) = \mathscr{D}_e[1-(R_e/R)^n]^2;$$

when $n = 6$, this is the Lennard-Jones (1924) (6–12)-potential function, whereas when $n = 1$, this is the Kratzer (1920) potential. For this potential the coefficients are

$$c_0 = n^2\mathscr{D}_e,$$

$$c_k = 2^{-k}(k+1) + \sum_{j=0}^{k-1} \frac{2^{1-j}(k+1)!\,(-1)^j}{j!(k+1-j)!\,(j+2)!\,n}\left[\frac{(2n+j+1)!}{(2n)!} - \frac{(n+j+1)!}{n!}\right], \quad k > 0.$$

The coefficients c_k converge fairly slowly but have alternating signs; in contrast the coefficients a_k diverge rapidly with increase of either k or n, also with alternating sign along the series. In the $U(y)$ function, after $2(n-1)$ converging coefficients of alternating signs the succeeding coefficients b_k become identically zero.

Coefficients according to any other desired model potential may be determined by comparison of $(\mathrm{d}^m U/\mathrm{d}R^m)_{R=R_\mathrm{e}}$ for that function with $(\mathrm{d}^m U(z)/\mathrm{d}R^m)_{R=R_\mathrm{e}}$.

For real molecules, at least four methods exist for the determination of the potential energy coefficients c_k for $U(z)$. The formal interconversion with respect to a_k or b_k can be effected through the following relations, for $k > 0$:

$$c_k = \sum_{i=0}^{k-1} (2^{-i}) \binom{k+1}{i} a_{k-1} + 2^{-k}(k+1),$$

$$a_k = \sum_{i=0}^{k-1} (-1)^i (2^{-i}) \binom{k+1}{i} c_{k-i} + (-1)^k 2^{-k}(k+1),$$

$$c_k = \sum_{i=0}^{k-1} (-1)^i (2^{-i}) \binom{k+1}{i} b_{k-i} + (-1)^k 2^{-k}(k+1),$$

$$b_k = \sum_{i=0}^{k-1} (2^{-i}) \binom{k+1}{i} c_{k-i} + 2^{-k}(k+1),$$

in which $\binom{m}{n}$ is the combinatorial $m!/(n!\,(m-n)!)$.

Alternatively the coefficients c_k may be determined from the Dunham energy coefficients Y_{LK} that result from a vibration–rotational analysis of discrete line spectra, for which

$$E(v, J) = \sum_{L=0} \sum_{K=0} Y_{LK}(v+\tfrac{1}{2})^L (J^2+J)^K.$$

Such a procedure depends on the energy coefficients Y_{LK} being expressed in terms of the potential coefficients c_k. We have derived expressions for $Y_{LK}, L+K \leqslant 6$, including terms up to c_8, except Y_{33} and Y_{24}. By this means, we have been able to determine sets of c_k for many diatomic molecules, including both ground and some excited electronic states, for which abundant spectroscopic data exist (as Y_{LK}). Because of the nonlinear dependence of Y_{LK} on c_k, the method is iterative, until self-consistency is achieved, which is entirely analogous to the earlier determination of a_i (Ogilvie & Koo 1976), including full statistical analysis of error propagation and correlation. Comparison of the results from the same set of Y_{LK} for these molecules according to the same test of convergence demonstrates that fewer iterations are required (typically about one third fewer) for the c_k than for the a_k. With sufficient numerical precision carried through all computations, the c_k obtained directly from the Y_{LK} agree perfectly with those obtained via the a_k and the above interconversion relations. The set of seven, or nine, c_k ($0 \leqslant k \leqslant 6$ or 8) can be further applied to the prediction of other Y_{LK} not used in the determination of the c_k. The sets of such Y_{LK}, their estimated standard deviations and correlation coefficients, as predicted though the c_k, are practically identical with those analogously predicted through the a_k, as expected because the $Y_{LK}(c)$ were transformed from the $Y_{LK}(a)$. Because of experimental inaccuracy inevitably present in determination of line frequency, and because of the finite number of lines measurable for any molecule, the calculated Y_{LK} derived from a fitting routine differ from the 'physical' Y_{LK};

TABLE 1. POTENTIAL ENERGY PARAMETERS OF SOME HYDRIDES IN $X\ ^1\Sigma$ STATES(1)

	HF(2)	HCl(3)	HBr(4)	HI(5)	H_2(6)
$c_0/10^{-18}$ J	4.06044	4.19378	4.11779	4.066167	1.57927
$\sigma/10^{-22}$ J	±0.0028	±0.3	±1.2	±0.34	±0.30
c_1	−1.253420	−1.3629947	−1.436359	−1.546119	−0.592838
	$\pm 6.7\times10^{-7}$	$\pm 1.9\times10^{-4}$	$\pm 4.0\times10^{-4}$	$\pm 3.2\times10^{-4}$	$\pm 4.6\times10^{-4}$
c_2	0.835257	0.866748	0.938771	0.98196	0.195581
	$\pm 2.2\times10^{-6}$	$\pm 6.3\times10^{-4}$	$\pm 3.1\times10^{-3}$	$\pm 1.4\times10^{-3}$	$\pm 5.5\times10^{-3}$
c_3	−1.761453	−0.49804	−0.56019	−0.67305	−0.37431
	$\pm 5\times10^{-6}$	$\pm 5.5\times10^{-3}$	±0.050	±0.013	$\pm 8.6\times10^{-3}$
c_4	−0.86357	0.1727	−0.1468	0.6754	0.5832
	$\pm 1.1\times10^{-5}$	±0.029	±0.23	±0.097	±0.013
c_5	−1.33865	0.2687	1.3143	−0.9333	−1.1722
	$\pm 2.9\times10^{-5}$	±0.044	±0.91	±0.24	±0.079
c_6	17.195	−1.977	−1.776	−11.02	2.331
	$\pm 8.4\times10^{-5}$	±0.29	±7.0	±1.0	±0.68
c_7	−40.8160	2.78	−9.71	61.0	—
	$\pm 2.5\times10^{-4}$	±1.1	±24	±6.4	—
c_8	−7.7354	4.89	55.07	−84.4	—
	$\pm 7.1\times10^{-4}$	±2.4	±47	±16.3	—
ω_e/m^{-1}	413925.925	299095.95	264931.61	230903.92	439948.66
σ/m^{-1}	±0.01	±0.01	±3.8	±0.89	±4.1
B_e/m^{-1}	2095.5386	1059.3478	846.5002	651.1861	6086.542
σ/m^{-1}	$\pm 1\times10^{-4}$	$\pm 1.4\times10^{-3}$	$\pm 1.9\times10^{-3}$	$\pm 8.3\times10^{-3}$	±0.097
$\gamma_e/10^{-2}$	1.01251866	0.7083665	0.639033	0.564027	0.76693
$\sigma/10^{-7}$	±0.054	±0.17	±0.84	±0.16	±6.6
$k_e/(\text{N m}^{-1})$	966.1303	516.321	411.652	314.100	574.662
$\sigma/(\text{N m}^{-1})$	$\pm 4.7\times10^{-5}$	$\pm 3.4\times10^{-3}$	±0.012	$\pm 2.4\times10^{-3}$	±0.011
$R_e/10^{-12}$ m	91.61894	127.45536	141.4432	160.9056	74.13737
$\sigma/10^{-16}$ m	±0.022	±0.81	±1.6	±1.0	±5.9
$\mathcal{D}_e/10^{-19}$ J	9.81001	7.3984	6.2806	5.12063	7.60763
$\sigma/10^{-21}$ J	±1.2	±0.22	±0.35	±1.4	±0.01

(1) In this and succeeding tables $\gamma_e = 2B_e/\omega_e$ and $k_e = 4\pi^2c^2\omega_e^2m_1m_2/(m_1+m_2)$. All the $\mathcal{D}_e$-values in tables 1–5 come from a combination of the spectroscopic data for zero-point energy and the best thermodynamic or spectroscopic data for $\mathcal{D}_0$.

(2) Y_{LK} from Huffaker (1977); standard deviations of these were not given, so were here estimated (probably underestimated).

(3) Y_{LK} for $H^{35}Cl$ from Coxon & Ogilvie (1981, manuscript in preparation for publication).

(4) Y_{LK} for $H^{81}Br$ from Niay *et al.* (1977).

(5) Y_{LK} from Guelachvili *et al.* (1981).

(6) Y_{LK} from Buijs & Gush (1971), except Y_{40}, estimated to be -3.0 ± 1.3 m^{-1}.

this effect is particularly discernible in values of the less accurate Y_{LK}, such as $Y_{41}, Y_{51}, Y_{40}, Y_{50}$, resulting from successive determinations incorporating new experimental data (further line frequencies). Naturally this uncertainty affects the accuracy of determination of the higher a_k or c_k (c_6, c_7, c_8 etc.), but also affects to a small extent the lower a_k or c_k because of the complicated dependence of Y_{LK} on

TABLE 2. POTENTIAL ENERGY PARAMETERS OF SOME FURTHER HYDRIDES

	LiH X⁽¹⁾	NaH X⁽²⁾	NaH A⁽³⁾	OH X⁽⁴⁾	OH A⁽⁵⁾
$c_0/10^{-18}$ J	1.306495	1.39053	0.28639	3.67288	2.89199
$\sigma/10^{-22}$ J	±0.255	±3.1	±0.33	±0.196	±9.9
c_1	−0.91026	−1.12648	−1.49313	−1.26062	−1.4874
	$\pm 1.4\times10^{-4}$	$\pm 9.3\times10^{-4}$	$\pm 9.2\times10^{-4}$	$\pm 7.3\times10^{-5}$	±0.011
c_2	0.37545	0.55586	3.3518	0.75574	1.1485
	$\pm 5.8\times10^{-4}$	$\pm 3.6\times10^{-3}$	$\pm 7.2\times10^{-3}$	$\pm 4.6\times10^{-4}$	±0.054
c_3	−0.03537	0.1665	−17.963	−0.4284	−0.9698
	$\pm 1.4\times10^{-3}$	$\pm 8.6\times10^{-3}$	±0.038	$\pm 1.8\times10^{-3}$	±0.18
c_4	−1.1588	−1.437	86.853	0.1742	−3.91
	$\pm 4.1\times10^{-3}$	±0.021	±0.27	±0.010	±0.71
c_5	3.1623	1.927	−364.32	0.1335	20.27
	±0.060	±0.059	±1.25	±0.047	±2.6
c_6	−7.145	0.632	1602.9	−1.4786	−18.48
	±0.32	0.27	±7.4	±0.063	±11.8
c_7	—	—	—	2.535	—
	—	—	—	±0.24	—
c_8	—	—	—	0.510	—
	—	—	—	±0.91	—
ω_e/m^{-1}	140616.5	117154.0	31474.0	373786.53	318195.42
σ/m^{-1}	±1.0	±5.0	±1.6	±0.086	±2.5
B_e/m^{-1}	751.6033	490.182	171.778	1889.13985	1738.660
σ/m^{-1}	±0.010	±0.010	±0.0102	$\pm 4.05\times10^{-3}$	±0.54
$\gamma_e/10^{-2}$	1.06901	0.83682	1.09155	1.010812	1.092825
$\sigma/10^{-7}$	±1.6	±17.4	9.0	±0.27	±35.6
$k_e/(\mathrm{N\ m^{-1}})$	102.664	78.0765	5.6352	780.57	565.574
$\sigma/(\mathrm{N\ m^{-1}})$	$\pm 1.5\times10^{-3}$	$\pm 6.7\times10^{-3}$	$\pm 5.7\times10^{-4}$	$\pm 3.6\times10^{-4}$	±0.087
$R_e/10^{-12}$ m	159.536	188.732	318.816	97.01614	101.1273
$\sigma/10^{-16}$ m	±10.6	±192	±94.4	±1.04	±157
$\mathscr{D}_e/10^{-19}$ J	4.03043	3.491	1.85	7.40353	5.401
$\sigma/10^{-21}$ J	±0.03	35	20	±0.8	±54

(1) Y_{LK} for ^{7}LiH $X\,^1\Sigma$ from Orth & Stwalley (1979); standard deviations were not given, so were here estimated.

(2) Y_{LK} for NaH $X\,^1\Sigma^+$ from Orth *et al.* (1980); standard deviations were not given, so were here estimated.

(3) Y_{LK} for NaH $A\,^1\Sigma^+$ from Orth *et al.* (1980); only Y_{10}–Y_{40} and Y_{01}–Y_{31} were used, and standard deviations were here estimated.

(4) Y_{LK} for OH $X\,^2\Pi$ from Coxon (1980).

(5) Y_{LK} for OH $A\,^2\Sigma^+$ from Barrow (1956).

these coefficients. The combination of these two effects, namely the distinction between calculated and true 'physical' Y_{LK}, and the sensitivity of lower a_k or c_k to the higher Y_{LK}, causes an uncertainty in the value of other Y_{LK}, $K > 1$, beyond what is either calculated during the spectral analysis or predicted through the potential energy coefficients; for this reason there is difficulty in incorporation of such predicted Y_{LK} into the spectral analysis process. Some sets of c_k for various molecules, derived from the indicated source of Y_{LK}, are presented in tables 1–5.

TABLE 3. POTENTIAL ENERGY PARAMETERS OF SOME NON-HYDRIDES

	CN X⁽¹⁾	CN A⁽¹⁾	CO X⁽²⁾	CS X⁽³⁾	NO X⁽⁴⁾
$c_0/10^{-18}$ J	11.18726	9.516095	12.1066291	10.00224	10.561362
$\sigma/10^{-22}$ J	± 0.906	± 1.04	± 0.0065	± 0.25	± 0.047
c_1	− 1.66009	− 1.76757	− 1.697174	− 1.885338	− 1.915556
	$\pm 4.0 \times 10^{-4}$	$\pm 5.2 \times 10^{-4}$	$\pm 4.6 \times 10^{-5}$	$\pm 5.5 \times 10^{-5}$	$\pm 3.6 \times 10^{-5}$
c_2	0.9985	1.2095	1.210610	1.54239	1.49198
	$\pm 2.5 \times 10^{-3}$	$\pm 3.7 \times 10^{-3}$	$\pm 2.5 \times 10^{-5}$	$\pm 7.3 \times 10^{-4}$	$\pm 2.4 \times 10^{-4}$
c_3	− 0.3210	− 0.57302	− 0.50467	− 0.6843	− 0.4121
	± 0.038	± 0.052	$\pm 2.9 \times 10^{-4}$	$\pm 4.4 \times 10^{-3}$	$\pm 4.4 \times 10^{-3}$
c_4	0.1143	0.8331	0.3269	0.0727	− 0.0625
	± 0.28	± 0.38	$\pm 2.0 \times 10^{-3}$	± 0.046	± 0.035
c_5	− 1.776	− 2.666	0.01368	0.1693	− 1.3254
	± 1.67	± 5.1	$\pm 8.9 \times 10^{-3}$	± 0.29	± 0.27
c_6	—	—	− 1.3231	—	− 3.49
	—	—	± 0.041	—	± 2.2
ω_e/m^{-1}	206869.41	181326.74	216981.522	128515.49	190412.17
σ/m^{-1}	± 0.64	± 0.84	$\pm 4.0 \times 10^{-3}$	± 0.16	± 0.039
B_e/m^{-1}	189.9732	171.5887	193.128318	82.00446	170.48775
σ/m^{-1}	$\pm 1.0 \times 10^{-3}$	$\pm 1.0 \times 10^{-3}$	$\pm 7.7 \times 10^{-6}$	$\pm 2.75 \times 10^{-6}$	$\pm 3.1 \times 10^{-5}$
$\gamma_e/10^{-2}$	0.183665	0.189259	0.178013608	0.1276180	0.1790723
$\sigma/10^{-7}$	± 0.113	± 0.14	$\pm 7.8 \times 10^{-3}$	± 0.016	± 0.051
$k_e/(\mathrm{N\ m}^{-1})$	1629.394	1251.864	1901.88004	849.0625	1594.9834
$\sigma/(\mathrm{N\ m}^{-1})$	± 0.010	± 0.012	$\pm 6.9 \times 10^{-5}$	$\pm 2.1 \times 10^{-3}$	$\pm 6.5 \times 10^{-4}$
$R_e/10^{-12}$ m	117.182	123.301	112.8327195	153.4948	115.0792
$\sigma/10^{-16}$ m	± 3.1	± 3.6	± 0.02	± 0.26	± 0.11
$\mathscr{D}_e/10^{-19}$ J	12.6616	11.1598	18.01246	11.91113	10.6126
$\sigma/10^{-21}$ J	± 30	± 30	± 0.4	± 2.1	± 0.5

(1) Y_{LK} for CN $X\,^2\Sigma^+$ and $A\,^2\Pi$ states from Kotlar *et al.* (1980).
(2) Y_{LK} for CO $X\,^1\Sigma$ from Dale *et al.* (1979).
(3) Y_{LK} for CS $X\,^1\Sigma$, Y_{10}–Y_{30} from Todd & Olson (1979); Y_{01}–Y_{31} from Bustreel *et al.* (1979).
(4) Y_{LK} for NO $X\,^2\Pi$ from Hallin *et al.* (1979).

A further method of determination of the potential coefficients is by direct derivation from measured frequencies of spectral lines, a nonlinear process not involving the intermediacy of Y_{LK} (Niay *et al.* 1977). This method has been directly applied to a_k-determination, but not to c_k-determination in the present work. In view of documented difficulties in the fitting of Y_{LK} to the observed transition frequencies (Woolley 1976) the procedure of fitting directly to potential coefficients seems to be the preferred method of spectroscopic analysis, if possible by treating concurrently all available data from isotropic molecules (Dale *et al.* 1979). The principal impediment to such a procedure is at present the limited set of Y_{LK} available.

The fourth method of determination of potential energy coefficients is by fitting potential energy curves or points arising from other experimental or theoretical data. For instance *ab initio* quantum computations, or numerical methods (such as R.K.R.) from spectral data (Goodisman 1973), may be the origin of such sets of

TABLE 4. POTENTIAL ENERGY PARAMETERS OF SOME HOMONUCLEAR MOLECULES

	Na_2 X$^{(1)}$	Na_2 B$^{(1)}$	Mg_2 X$^{(2)}$	Ar_2 X$^{(3)}$
$c_0/10^{-18}$ J	0.81282	0.61076	0.13965	0.083973
$\sigma/10^{-22}$ J	±0.43	±3.4	±0.67	±6.1
c_1	−0.96785	−0.95603	−3.5909	−7.0165
	$\pm 7.5 \times 10^{-4}$	±0.017	$\pm 9.5 \times 10^{-3}$	±0.092
c_2	−0.48819	−1.1199	8.4979	35.185
	$\pm 2.8 \times 10^{-3}$	±0.061	±0.101	±2.2
c_3	1.0749	−4.942	−14.29	−120.1
	±0.021	±0.38	±0.73	±33.5
c_4	−1.5342	23.04	−17.25	−520.1
	±0.095	±1.8	±6.2	±322
c_5	−7.574	36.66	261.3	15044
	±0.33	±5.7	±45.7	±2650
c_6	35.965	−288.0	−945.6	−166850
	±1.5	±26.6	±302	±31600
c_7	−7.142	−69.4	—	—
	±4.23	±112	—	—
c_8	−243.1	1587	—	—
	±12.6	±320	—	—
ω_e/m^{-1}	15912.26	12407.8	5111.74	3183.59
σ/m^{-1}	±0.15	±2.8	±1.2	±11.5
B_e/m^{-1}	15.47060	12.5182	9.29228	5.9940
σ/m^{-1}	$\pm 7.6 \times 10^{-4}$	$\pm 4.1 \times 10^{-3}$	$\pm 7.2 \times 10^{-4}$	$\pm 2.4 \times 10^{-3}$
$\gamma_e/10^{-2}$	0.194445	0.20180	0.363566	0.37656
$\sigma/10^{-7}$	±0.97	±7.9	±9.2	±136
$k_e/(N\ m^{-1})$	17.1490	10.427	1.8463	1.1932
$\sigma/(N\ m^{-1})$	$\pm 3.3 \times 10^{-4}$	$\pm 4.7 \times 10^{-3}$	$\pm 8.8 \times 10^{-4}$	$\pm 8.6 \times 10^{-3}$
$R_e/10^{-12}$ m	307.889	342.276	388.941	375.172
$\sigma/10^{-16}$ m	±75.7	±560	±150	±753
$\mathscr{D}_e/10^{-19}$ J	1.1700	0.6138	0.085188	0.019775
$\sigma/10^{-21}$ J	±1.4	±1.4	±0.015	±0.012

(1) Y_{LK} for Na_2 $X\,^1\Sigma_g^+$ and $B\,^1\Pi_u$ from Demtroder & Stock (1975).
(2) Y_{LK} for Mg_2 $X\,^1\Sigma_g^+$ from Vidal & Scheingraber (1977).
(3) Y_{LK} fitted here to spectroscopic data of Colburn & Douglas (1976).

points for either ground or excited electronic states. Monitored by standard statistical tests of significance, fitting these points directly to the $U(z)$ function will generate the c_k coefficients. Alternatively other types of continuous curves from thermodynamic or transport properties, such as the potential function for Ar_2 (Barker *et al.* 1971), might be transformed by equating derivatives as specified above. As an indication of the relative merits of fitting $U(x)$, $U(y)$ or $U(z)$, we can take as reference the R.K.R. points for HF (Huffaker 1977); when these were fitted by the same least-squares routine, the definition of the coordinate transformation merely being changed from R to x, y or z, an F-value (statistical distribution function taken as a measure of goodness of fit (Kendall & Stuart 1979) of 10^6 was reached with

TABLE 5. POTENTIAL ENERGY PARAMETERS OF SOME MASSIVE NON-HYDRIDES

	Cs_2 X(1)	BiI X(2)	I_2 X(3)	I_2 B(3)
$c_0/10^{-18}$ J	0.74831	4.9141	6.11574	2.704130
$\sigma/10^{-22}$ J	± 0.341	± 120	± 0.17	± 0.043
c_1	-1.3433	-2.577	-2.91849	-3.528971
	$\pm 2.6 \times 10^{-3}$	$\pm 3.1 \times 10^{-3}$	$\pm 7.7 \times 10^{-5}$	$\pm 2.8 \times 10^{-6}$
c_2	-0.64864	3.529	3.23326	2.56427
	± 0.011	± 0.055	$\pm 3.8 \times 10^{-3}$	$\pm 3.6 \times 10^{-5}$
c_3	4.7102	-3.054	-2.763	-71.7656
	± 0.73	± 0.35	± 0.029	$\pm 3.7 \times 10^{-4}$
c_4	-13.815	-229.3	-11.36	952.309
	± 4.2	± 44.3	± 0.14	$\pm 3.6 \times 10^{-3}$
c_5	31.13	2158.9	38.55	11785.78
	± 12.2	± 416	± 0.69	± 0.018
c_6	-140	—	—	-255350
	± 41.5	—	—	± 0.66
c_7	—	—	—	-125846
	—	—	—	± 2.2
c_8	—	—	—	2.566×10^7
	—	—	—	± 85
ω_e/m^{-1}	4202.686	16413	21451.94	12564.96
σ/m^{-1}	± 0.011	± 20	± 0.030	± 0.010
B_e/m^{-1}	1.17218	2.72228	3.736869	2.89947
σ/m^{-1}	$\pm 5.3 \times 10^{-5}$	$\pm 4.5 \times 10^{-7}$	$\pm 3.0 \times 10^{-7}$	$\pm 1.0 \times 10^{-9}$
$\gamma_e/10^{-2}$	0.0557825	0.033173	0.034839	0.0461516
$\sigma/10^{-7}$	± 0.25	± 4.04	$\pm 4.9 \times 10^{-3}$	$\pm 3.7 \times 10^{-3}$
$k_e/(N\ m^{-1})$	6.91544	125.315	172.042	59.0233
$\sigma/(N\ m^{-1})$	$\pm 3.8 \times 10^{-5}$	± 0.31	± 0.005	$\pm 9.4 \times 10^{-5}$
$R_e/10^{-12}$ m	465.207	280.051	266.638	302.7033
$\sigma/10^{-16}$ m	± 105	± 0.23	± 0.11	± 0.00053
$\mathscr{D}_e/10^{-19}$ J	0.63508	4.167	2.49268	0.870334
$\sigma/10^{-21}$ J	± 1.6	± 40	± 0.02	± 0.0003

(1) Y_{10}–Y_{40} from Benedict *et al.* (1977); Y_{01}–Y_{31} from Raab *et al.* (1979).

(2) Y_{LK} from Kuijpers *et al.* (1976).

(3) Y_{LK} from Luc (1980) for both $X\,^1\Sigma_g^+$ and $B\,^3\Pi_{0^+u}$ states of $^{127}I_2$; standard deviations estimated here.

degrees of polynomial of 8, 7 and 5 for the x, y, and z representations respectively. In some other cases, the y and z representations were found to be both markedly superior to that in x. Thus the coefficients c_k constitute an economical and accurate representations of the interatomic potential energy over a broad range of separation.

GENERATION OF FURTHER COEFFICIENTS

Because z remains finite as $R \to \infty$, boundary conditions may be used to produce coefficients beyond those defined from, for instance, limited spectroscopic data, just as for the $U(y)$ function (Simons *et al.* 1973). The applicable condition is that

$$[(R^2\,d/dR)^p\,U(R)] \to 0 \quad \text{as} \quad R \to \infty,$$

for values of p less than the exponent of limiting behaviour at large R. For such behaviour according to R^{-6}, the following five sum rules apply for a finite set of coefficients, n in number:

$$\sum_{i=1}^{n}(i+2)\,c_i\,2^{i-1}+1=0,$$

$$\sum_{i=1}^{n}(i+2)^2\,c_i\,2^{i-2}+1=0,$$

$$\sum_{i=1}^{n}(i+2)\,(i^2+4i+\tfrac{9}{2})\,c_i\,2^i/9+1=0,$$

$$\sum_{i=1}^{n}(i+2)\,(i^3+6i^2+14i+12)\,c_i\,2^{i-3}/3+1=0,$$

$$\sum_{i=1}^{n}(i+2)\,(i^4+8i^3+29i^2+52i+\tfrac{75}{2})\,c_i\,2^i/75+1=0.$$

The finite value of $U(z)$, namely $\mathscr{D}_\mathrm{e}$, as $R\rightarrow\infty$ or $z\rightarrow 2$, permits another condition:

$$4c_0\left(1+\sum_{i=1}^{n}c_i\,2^i\right)=\mathscr{D}_\mathrm{e}.$$

False minima in the region $10^{-14}<R/\mathrm{m}<10^{-11}$, are avoided if coefficients c_k with odd subscripts $(1, 3, 5, \ldots)$ have negative signs whereas c_k with even subscripts have positive signs. Use of these equations to generate six additional coefficients results in spurious maxima or minima in $U(z)$ in the region $0.8<z<2$, just as previously encountered in the $U(y)$ function (Simons *et al.* 1973), but one should not expect any function to be accurate beyond its range of definition.

DISCUSSION

Let us consider a potential energy function of a general type of truncated polynomial,

$$U(w_{mn})=d_0^{mn}\,w_{mn}^2\,(1+\sum_{i=1}d_i^{mn}\,w_{mn}^i),$$

in which the argument w_{mn} becomes a function of two integer parameters m and n as well as of R and R_e:

$$w_{mn}=(m+n)\,(R-R_\mathrm{e})/(mR+nR_\mathrm{e}).$$

These relations define a family of functions, of which the case $n=0$ corresponds to $U(x)$, $m=0$ corresponds to $U(y)$, and $m=n\neq 0$ corresponds to $U(z)$, as described earlier. To investigate the relative suitability of members of this family to fit a particular molecule, we can select the diargon potential (Aziz & Chen 1977), fairly accurately known over a range of internuclear separation of about three, and including not only the binding region ($U<\mathscr{D}_\mathrm{e}$) but also the repulsive curve up to $U\approx 6000\mathscr{D}_\mathrm{e}$. A sample of 85 points in the range $2.5<R/10^{-10}\,\mathrm{m}<6.7$, with geometrically increasing interval, was used in a general routine LMM1 for fitting parameters (Osborne 1976) in which the same initial estimates of parameters d_i^{mn} were applied to each set of m and n. Two sets of coefficients, numbering either seven ($d_0^{mn}-d_6^{mn}$) or nine ($d_0^{mn}-d_8^{mn}$), were tested. After convergence according to a specified criterion, we can take the number of iterations and the sum of the squared deviations from the reference $U(R)$ to serve as indicators of the relative ease and goodness of fit, respectively. These results, and the limiting values of w_{mn} corresponding to $R = 0$ and $R \rightarrow \infty$, are displayed in table 6. These data demonstrate that the $U(y)$-representation is slightly superior in these cases to that of $U(z)$, but that four times as many iterations are required. In fact neither of these representations is absolutely the best, but the case $m = 4$, $n = 1$ is best for determination of seven coefficients, whereas the case $m = 4$, $n = 3$ proves best for the set of nine coefficients. Conversion of the resulting coefficients to those of the $U(z)$-function may be easily accomplished according to the relations

$$d_0^{mn} = c_0, \quad c_1 = d_1^{mn} + (n-m)/(n+m),$$

$$c_k = (k+1)\left[\left(\frac{-m}{m+n}\right)^k - \frac{1}{(-2)^k}\right] + d_k^{mn} + \sum_{i=1}^{k-1} \binom{k+1}{i+1} \left[\left(\frac{-m}{m+n}\right)^{k-i} d_i^{mn} - \frac{c_i}{(-2)^{k-i}}\right],$$

$k > 1$. The important conclusion of this section is that $U(z)$, as a member of a new family of polynomial potential functions defined according to the equation for $U(w_{mn})$ above, is a generally useful and justifiable form of function. In particular cases, the use of other members of the family, although not $U(x)$, may prove advantageous, but only the $w_{11} \equiv z$ parameter possesses the desirable equivalence of magnitude of limiting values (corresponding to $R = 0$ and $R \rightarrow \infty$) that ensures convergence within the entire range of accessible, real internuclear separation.

From the tables of sets of coefficients c_i, we can see that the magnitudes of $c_1, \ldots, c_5$ for the hydrogen halides are smaller than unity, and show similar trends to the sets of a_i published previously (Ogilvie & Koo 1976; Ogilvie 1978). In the excited electronic states, the corresponding c_i are almost invariably of larger magnitude than those for the ground state. Similarly there is a trend of increasing magnitudes of c_i with increasing reduced mass for the ground electronic state of molecules. The sets of c_i for the four isotopic molecules $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{13}C^{18}O$ are practically identical, but this result might be expected because the Y_{LK} for all these molecules were collectively determined (Dale *et al.* 1979).

Another approach to the improvement of potential energy functions of diatomic molecules has been to add and subtract the internuclear coulomb repulsion term to and from the potential function, one singularity that may limit convergence of the function thus being removed (Wu & Beckel 1973). Following preliminary announcement of the present work (J. F. Ogilvie, unpublished report, Research School of Chemistry, Australian National University, March 1974; paper presented at Canadian Spectroscopy Symposium, Ottawa, Canada, October 1974 (unpublished); paper ΣS4 presented at Molecular Spectroscopy Symposium, Columbus, U.S.A., June 1976 (unpublished)) the results of Engelke (1978, 1979) have demon-

TABLE 6. RESULTS OF LEAST-SQUARES ANALYSES OF POTENTIAL ENERGY FUNCTION OF Ar_2 X $^1\Sigma_g^+$ (AZIZ & CHEN 1977) FOR VARIOUS ARGUMENTS w_{mn} OF THE GENERAL POTENTIAL FUNCTION

(The limiting values of w_{mn} at $R = 0$ and $R \to \infty$, and the number of iterations N_{i+} and sum of squared deviations in the fit S_{sq}/m^{-2} for either seven- or nine-parameter potential functions are given for selected values of m and n.)

				7 parameters		9 parameters	
m	n	w_{mn} at $R = 0$	w_{mn} as $R \to \infty$	N_{i+}	S_{sq}	N_{i+}	S_{sq}
0	1	-1	∞	24	1.3×10^8	33	5.6 ± 10^5
1	0	$-\infty$	1	72	3960	85	7.4
1	1	-2	2	16	1.8×10^4	18	50.8
1	2	$-\frac{3}{2}$	3	21	3.6×10^5	21	800
1	3	$-\frac{4}{3}$	4	22	2.8×10^6	20	180
1	4	$-\frac{5}{4}$	5	20	7.5×10^6	23	1500
2	1	-3	$\frac{3}{2}$	17	1.3×10^4	29	21
2	3	$-\frac{5}{3}$	$\frac{5}{2}$	18	3.0×10^4	19	480
3	1	-4	$\frac{4}{3}$	55	1240	42	16
3	2	$-\frac{5}{2}$	$\frac{5}{3}$	16	2.5×10^4	18	8.4
3	4	$-\frac{7}{4}$	$\frac{7}{3}$	19	7400	19	310
4	1	-5	$\frac{5}{4}$	58	260	60	10
4	3	$-\frac{7}{3}$	$\frac{7}{4}$	17	2.7×10^4	18	3.6
5	1	-6	$\frac{6}{5}$	69	1470	71	8.3
5	4	$-\frac{9}{4}$	$\frac{9}{5}$	16	2.7×10^4	18	4.2
6	1	-7	$\frac{7}{6}$	69	2720	74	8.2
6	5	$-\frac{11}{5}$	$\frac{11}{6}$	16	2.7×10^4	18	6.6

strated that a potential function equivalent to $U(z)$ without the coulomb repulsion produced the best representation of the potential energy over the entire range of R in which it could be tested, without the necessity of knowing the dissociation energy.

For representing the potential energy and for relating the potential energy coefficients to the energy coefficients Y_{LK}, the more complicated functions of Thakkar (1975) and Engelke (1979), involving a variable exponent parameter in the argument of a truncated polynomial of type $U(w)$, would seem to have no real advantage over the present family of potential functions $U(w_{mn})$, specifically the $U(z)$ representation.

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REFERENCES

Aziz, R. A. & Chen, H. H. 1977 *J. chem. Phys.* **67**, 5719.
Barker, J. A., Fisher, R. A. & Watts, R. O. 1971 *Molec. Phys.* **21**, 657.
Barrow, R. F. 1956 *Ark. Fys.* **11**, 281.
Beckel, C. L. 1976 *J. chem. Phys.* **65**, 4319.
Benedict, R. P., Drummond, D. L. & Schlie, L. A. 1977 *J. chem. Phys.* **66**, 4600.
Born, M. & Oppenheimer, J. R. 1927 *Annln Phys.* **84**, 457.
Buijs, H. L. & Gush, H. P. 1971 *Can. J. Phys.* **49**, 2366.
Bustreel, R., DeMuynk-Marliere, C., DesTombes, J. L. & Journel, G. 1979 *Chem. Phys. Lett.* **67**, 178.
Colburn, E. A. & Douglas, A. E. 1976 *J. chem. Phys.* **65**, 1741.
Coxon, J. A. 1980 *Can. J. Phys.* **58**, 933.
Dale, R. M., Herman, M., Johns, J. W. C., McKellar, A. R. W., Nagler, S. & Strathy, I. K. M. 1979 *Can. J. Phys.* **57**, 677.
Demtroder, W. & Stock, M. 1975 *J. molec. Spectrosc.* **55**, 476.
Dunham, J. L. 1932 *Phys. Rev.* **41**, 721.
Engelke, R. 1978 *J. chem. Phys.* **68**, 3514.
Engelke, R. 1979 *J. chem. Phys.* **70**, 3745.
Goodisman, J. 1973 *Diatomic interaction potential theory.* London: Academic Press.
Guelachvili, G., Niay, P. & Bernage, P. 1981 *J. molec. Spectrosc.* **85, 253.**
Hallin, K. J., Johns, J. W. C., Lepard, D. W., Mantz, A. W., Wall, D. L. & Rao, K. N. 1979 *J. molec. Spectrosc.* **74**, 26.
Huffaker, J. N. 1977 *J. molec. Spectrosc.* **65**, 1.
Kendall, M. G. & Stuart, A. 1979 *The advanced theory of statistics.* London: Griffin.
Kotlar, A. J., Field, R. W., Steinfeld, J. I. & Coxon, J. A. 1980 *J. molec. Spectrosc.* **80**, 86.
Kratzer, A. 1920 *Z. Phys.* **3**, 289.
Kuijpers, P., Torring, T. & Dymanus, A. 1976 *Chem. Phys.* **12**, 309.
Lennard-Jones, J. E. 1924 *Proc. R. Soc. Lond.* A **106**, 463.
Luc, P. 1980 *J. molec. spectrosc.* **80**, 41.
Morse, P. M. 1929 *Phys. Rev.* **34**, 57.
Niay, P., Bernage, P., Coquant, C. & Fayt, A. 1977 *Can. J. Phys.* **55**, 1829.
Ogilvie, J. F. 1978 *J. molec. Spectrosc.* **69**, 169.
Ogilvie, J. F. & Koo, D. 1976 *J. molec. Spectrosc.* **61**, 332.
Orth, F. B. & Stwalley, W. C. 1979 *J. molec. Spectrosc.* **76**, 17.
Orth, F. B., Stwalley, W. C., Yang, S. C. & Hsieh, Y. K. 1980 *J. molec. Spectrosc.* **79**, 314.
Osborne, M. R. 1976 *J. Aust. math. Soc.* B **XIX**, 343.
Raab, M., Honing, G., Costell, R. & Demtroder, W. 1979 *Chem. Phys. Lett.* **66**, 307.
Simons, G., Parr, R. G. & Finlan, J. M. 1973 *J. chem. Phys.* **59**, 3229.
Thakkar, A. J. 1975 *J. chem. Phys.* **62**, 1693.
Todd, T. R. & Olson, W. B. 1979 *J. molec. Spectrosc.* **74**, 190.
Vidal, C. R. & Scheingraber, H. 1977 *J. molec. Spectrosc.* **65**, 46.
Wilson, E. B. 1979 *Int. J. Quantum Chem., Symp.* **13**, 5.
Woolley, R. G. 1976 *Adv. Phys.* **25**, 27.
Wu, F. M. & Beckel, C. L. 1973 *Int. J. Quantum Chem., Symp.* **7**, 135.