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SOME LIMITATIONS

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Analytic Potential Functions for Diatomic Molecules:
Some Limitations

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In discussions of the spectra of diatomic molecules, it is common in many physical chemistry and spectroscopy texts (1-4) to introduce the Morse(5) potential function

$$V(R) = D_e (1 - \exp(-\beta(R-R_e)))^2 \quad (1)$$

as representative of the real potential. The length scaling factor, β , is usually expressed in terms of the harmonic vibration constant, ω_e , the molecular reduced mass, μ , and the well depth, D_e , via

$$\beta = k \omega_e (2\pi^2 \mu / D_e)^{1/2} \quad (2)$$

where k is a collection of physical constants appropriate to the units used for ω_e , D_e , μ , and β . The Morse potential has the advantage that many simple, analytical expressions, such as eqn. (2), exist among the parameters of the potential function and observable spectroscopic constants. One may write the energy of a particular level with vibrational quantum number v and rotational quantum number J in the usual power series expression

$$G(v, J) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + B_v J(J+1) - D_e J^2 (J+1)^2 \quad (3)$$

where the rotational constant for vibrational level v is given by

$$B_v = B_e - \alpha_e (v + \frac{1}{2}) + \dots \quad (4)$$

(Only the first approximation to the centrifugal distortion constant, i.e., only D_e , is included in eqn. (3) for simplicity.)

Each of these molecular constants can be obtained, in principle,

from molecular spectra. Moreover, each can be related to the parameters of the Morse potential. In this paper, particular attention is given to the relationships between molecular constants and the dissociation energy, D_e .

The dissociation energy is often tacitly assumed to be calculable from spectroscopic constants and Morse function relations. It will be shown that not only are these calculations in poor agreement with known dissociation energies, but that there are in fact two independent ways of using spectroscopic constants and the Morse relations in such calculations. The most common approach is via

$$D_e = \omega_e^2 / 4\omega_e x_e \quad (5)$$

which is the basis of the linear Birge-Sponer (6) extrapolation method (which, in fact, preceded the discovery of the Morse function). Since the vibrational frequencies of the Morse oscillator are completely specified by the harmonic constant ω_e and the single anharmonic constant $\omega_e x_e$, eqn. (5) is exact for this oscillator. Equation (5) is often used, especially when other data are lacking.

One should also consider the Morse-Pekeris (7) expression for the vibration-rotation correction constant, α_e ,

$$\alpha_e = \frac{6}{\omega_e} ((\omega_e x_e B_e^3)^{1/2} - B_e^2). \quad (6)$$

One may solve eqn. (6) for the anharmonicity constant,

$$\omega_e x_e = (\alpha_e \omega_e / 6 + B_e^2)^2 / B_e^3, \quad (7)$$

and substitute this expression in eqn. (5), yielding

$$D_e = 9\omega_e^2 B_e^3 / (\alpha_e \omega_e + 6B_e^2)^2. \quad (8)$$

Equation (8) is more appropriate when accurate rotational constants are available(8). Nevertheless, if the molecule is truly a Morse oscillator, then both eqn. (5) and eqn.(8) should give the same answer for the dissociation energy.

In Table I, D_e 's predicted by eqn. (5) and eqn. (8) are compared to experimental values for a number of diatomic molecules. These molecules range from the most strongly bound to the most weakly bound, from triply-bonded to van der Waals bonded, and from stable molecules to free radicals. It can be seen from the Table that neither Morse value compares well with experiment, regardless of the molecular bonding in effect. The computed values tend to be higher than the experimental values, but by amounts which follow no obvious systematic trend. Note also that molecules which appear to be "good Morse oscillators" when comparing one column to experiment (such as H_2 or HCl), are, in fact, not at all good when experiment is compared to the other column.

It is also instructive to note that another simple diatomic potential function, the Lennard-Jones (2n,n) function

$$V(R) = D_e [1 + (R_e/R)^{2n} - 2(R_e/R)^n] \quad (9)$$

can be treated along the same lines as the Morse function. The (2n,n) potential is usually discussed in the context of weak intermolecular forces, such as one encounters in scattering, transport, or non-ideal gas discussions. For these cases, one usually takes $n = 6$ in order to mimic the R^{-6} dispersion or London attraction.

If we assume n to be simply a parameter, then one finds a relationship similar to eqn. (5),

$$D_e = \omega_e^2 / 4B_e n^2 . \quad (10)$$

Note, however, the appearance on the right-hand side of eqn. (10) of a potential parameter, n , as well as spectroscopic constants. The expressions from the Morse oscillator contained only observed quantities. It is interesting to note that an expression for D_e analogous to eqn. (8) can be derived. Using the relationship for the vibration-rotation correction of the $(2n,n)$ potential in analogy with the use of the Morse-Pekeris relation above, one obtains an expression for the $(2n,n)$ dissociation energy which depends only on spectral constants, not on potential parameters. The required expression is

$$\alpha_e = 6n(B_e^2 / \omega_e) , \quad (11)$$

which leads to

$$D_e = 9B_e^3 / \alpha_e^2 . \quad (12)$$

When eqn. (12) is applied to any of the molecules in Table I, the predicted dissociation energies are typically two to three times larger than the observed values. For weakly bonded molecules, (such as NaAr), the predictions of eqn. (12) are considerably better, but, in general, they are too high by about 30% (8).

In conclusion, it must be remembered that use of the Morse function or any other simple analytic potential function implies a series of constraining relations among the parameters of the function and the spectroscopic constants deduced from experiment. While these simple functions serve a valuable pedagogic link between the simple harmonic potential and the qualitative features of a real diatomic potential, students should not be given the impression that

the relations based on these functions, such as eqn. (5), are especially accurate or unique. While the dissociation energy has been emphasized here, a similar warning must be given whenever a particular spectral constant, such as α_e or D_e , is deduced from other constants, rather than directly measured.

Also, while the role of anharmonicity in decreasing the spacing between successively higher vibrational levels follows directly from elementary considerations of quantum theory, the anharmonicity constant is by no means a unique indicator of the qualitative shape of a diatomic molecule's potential energy function. In particular, the increase in average bond length with increasing vibrational quantum number as expressed by the constant α_e is an equally valid way of noting the same effect, as is shown by the appearance of α_e in eqn. (8) and again in eqn. (12).

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Table I. Dissociation energies predicted by Morse potential relationships and compared to experimental values. The energies are in eV units. Data taken from Huber and Herzberg (9).

Molecule	Eq. (5)	Eq. (8)	Experiment
CO	10.982	10.387	11.226
N ₂	12.037	11.793	9.905
NO	7.969	7.754	6.614
O ₂	6.460	5.874	5.213
HF	5.906	4.988	6.123
HCl	5.249	4.681	4.618
HBr	4.810	4.324	3.921
HI	4.168	3.884	3.196
OH	5.101	4.477	4.621
CH	4.020	3.563	3.640
F ₂	2.317	2.172	1.658
Cl ₂	3.630	3.578	2.514
Br ₂	3.044	3.146	1.991
I ₂	2.322	2.518	1.555
H ₂	4.948	3.822	4.747
Na ₂	1.081	1.309	0.730
He ₂ ⁺	2.533	2.517	2.469
NaAr ^a	4.82x10 ⁻³	4.86x10 ⁻³	5.14x10 ⁻³

^aData taken from reference (10).