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Systematic estimate of binding energies of weakly bound diatomic molecules

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There is often insufficient spectroscopic data for a full RKR inversion to yield a potential for weakly bound diatomic molecules. In these cases, parametrized functions such as the Morse or Thakkar potentials may be used to obtain estimates of the binding energy. The Thakkar potential is more flexible, and has been used successfully on some weakly bound systems. In the more usual case, the Thakkar parameter p, which determines long-range behavior R^{-p}, is chosen by $p = -a_1 - 1$, where a_1 is the first Dunham coefficient; p is usually noninteger. We present an alternative choice for p which makes systematic use of the determinable Thakkar coefficients $e_n(p)$; we choose p to be the minimum integer necessary to obtain monotonically decreasing positive values for the $e_n(p)$. This approach, which yields good estimates of known ground and excited state binding energies for numerous diatomic molecules, also produces physically meaningful R^{-6} long-range behavior for the known NaAr and NaNe potentials.

One of the more basic physical quantities important for descriptions of intermolecular or interatomic processes is the Born–Oppenheimer potential. The potentials are useful in understanding a wide range of processes including the formation of spectral line profiles and the rates of a large number of inelastic and elastic collision phenomena. They are also important in descriptions of radiative and optical collisions and in understanding the dynamical aspects of simultaneous strong collisional and radiative processes.

Interatomic potentials for a system of atoms or molecules may be obtained either by calculation using *ab initio*, model potential, or pseudopotential techniques, or by inversion of spectroscopic data. Our discussion here will be limited to those cases where discrete rotational and vibrational spectroscopic information is available for inversion, using suitable techniques, to obtain a portion of the interaction potential. The most commonly used approach is the RKR inversion,[1] which generates an inner and outer turning point for each eigenstate of vibrational motion. For those situations where large amounts of data are available, this is the method of choice. However, many times it happens that only a limited amount of spectroscopic data is obtainable from a fairly narrow portion (in R) of the interatomic potential.

Then it would be useful to have other approaches to analyze the data; ones which allow both an accurate description of the actual data and a reliable extrapolation to regions of the potential for which data is not available. Two situations commonly arise. When data are available from the long-range (LR) portion of the potential, where the interatomic forces are given by inverse powers of the internuclear separation, the LR analysis technique of LeRoy[2] makes predictions about the deeper regions of the potential. When data are from portions of the potential near its minimum, empirical multiparameter potential functions[3] are often used to extrapolate to the LR region and to estimate binding energies. However, these functions are often not flexible enough to even reproduce all the data from which they are derived, much less make reliable predictions about the LR portion of the potential.

A recently constructed potential function, the generalized Thakkar expansion,[4,5] seems flexible enough to overcome these difficulties and also is capable of yielding physically meaningful LR R^{-p} behavior (p is a real parameter in the Thakkar expansion). However, the customary choice of p ($p = -a_1 - 1$) in terms of the first Dunham[6] coefficient a_1 generally leads to noninteger values for this quantity. Furthermore, when the Thakkar expansion is applied to analysis of limited spectroscopic data, it often displays poor asymptotic properties.[7]

We present here a simple mathematical idea by which p can be chosen so as to eliminate the two undesirable properties of the customarily used Thakkar potential[5]; we select p to be the minimum integer such that the Thakkar coefficients form a monotone decreasing positive sequence. Our main goal is to obtain reliable values for the binding energy D_e, and our approach improves the asymptotic properties of the Thakkar series prediction of this quantity. Another attractive aspect of our approach is that the integer p so determined predicts the dominant long range R^{-p} behavior of the interatomic potential. This prediction can then be contrasted with what one might expect for the long-range behavior of the potential.

THEORY

The Thakkar expansion

The generalized expansion for a diatomic molecule devised by Thakkar[5] is written as

$$V(R) = e_0(p)\lambda^2\left[1 + \sum_{n=1}^{\infty} e_n(p)\lambda^n\right], \tag{1}$$

where

$$\lambda = s(p)\left[1 - (R_e/R)^p\right], \tag{2}$$

and where

$$s(p) = \begin{Bmatrix} +1 & p>0 \\ -1 & p<0 \end{Bmatrix}. \tag{3}$$

Here p is a nonzero real number, the $e_n(p)$ are real expansion coefficients, and R the internuclear separation. R_e is the equilibrium internuclear separation. Thakkar has shown

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that the form (1) can be obtained from a perturbation-theoretic expansion of a Born–Oppenheimer Hamiltonian. It has also been shown that different choices of p and selected e_n lead variously to the Lennard-Jones potential, the Dunham expansion, and the Kratzer–Fues potential.

In the LR region ($R \gg R_e$), Eq. (1) becomes[8]

$$V(R) \to D_e^T - (R_e/R)^p \left[e_0 \sum_{n=1}^{\infty} n e_n(p) + 2D_e^T \right], \tag{4}$$

where D_e^T is the Thakkar expression for the binding energy

$$D_e^T = e_0 \left[1 + \sum_{n=1}^{\infty} e_n(p) \right]. \tag{5}$$

As the next term in the expansion of $V(R)$ decreases as $(R_e/R)^{2p}$, the Thakkar expansion cannot be directly compared to a general multipole expansion of the interaction energy. However, we are concerned here primarily with the asymptotic properties of the Thakkar series prediction of D_e^T and with the leading term in the LR potential as in Eq. (4).

It has been suggested (but not proved) that the Thakkar expression[5] converges rapidly in the R interval $(R_e/2^{1/|p|}, \infty)$ when $p > 0$. This is in contrast to the Dunham[6] expansion, which converges to the RKR potential for $R < 2R_e$ but which diverges for $R > 2R_e$, and hence is not useful in analysis of data from the LR region (or for extrapolating to this region).

Thakkar has also shown that the expansion coefficients $e_n(p)$ are algebraically related to the Dunham expansion coefficients a_n and hence to the mechanical constants usually obtained in spectroscopic investigations. The quantity p is a parameter in these relationships and must be chosen by some appropriate algorithm. Thakkar suggested $p = -a_1 - 1$, where a_1 is the first Dunham coefficient. An immediate consequence of this choice, which has become customary, is $e_1(p) = 0$. This particular selection of p was motivated by the desire that the first order expansion of Eq. (1) about $R = R_e$ reproduce the force constants and that Eq. (1) represent a good zeroth order potential when only a few Dunham coefficients are known. However, there are two rather undesirable consequences of this selection for p. First, p is generally noninteger, leading to nonmultipole R^{-p} LR behavior of the potential. This is especially an issue for van der Waals diatomic molecules, where a fair portion of the potential should be of the R^{-p} form (with p an integer). Second, when limited amounts of spectroscopic data yield only a few of the e_n, the sequence of Thakkar coefficients $[e_n(p)]$ has poor asymptotic properties.[7] Also, because of severe limitations on the amount of data usually available, application of Padé approximant methods[7,9] does not seem to improve the situation.

To illustrate these points we present, in the second column of Table I, the results of a standard Thakkar analysis[7] for the ground state of the van der Waals molecule Ca_2. It is seen immediately that the value of p (3.56) is far from the physically expected value of 6 for this state. Furthermore, the magnitude of the individual e_n grows as n increases and it is not at all clear that a good approximation to the potential, or the binding energy, could be obtained from the sum of these terms. In fact, the last coefficient (e_6) is nearly 1.4 times the sum of all the other e_n. The effect of e_6 alone is to bring the prediction of the binding energy from 3348 to 1274.9 cm^{-1}, making the fair agreement between this value and the experimental one of 1095 cm^{-1} seem fortuitous.

The method

Our approach is designed specifically to overcome the difficulties discussed in the previous paragraphs. We make an alternative choice for p which makes systematic use of the determinable $e_n(p)$; we choose p to be the minimum integer necessary to obtain monotonically decreasing positive values for the $e_n(p)$. This, of course, automatically leads to improved asymptotic properties for $V(R)$ and for the prediction of D_e^T. The possibility now also exists that p takes on physically meaningful integer values; ones which can represent the leading term in the LR multipole expansion of $V(R)$. Note that our method of choosing p means that e_1 is generally nonzero, and that the exact relation between the potential and the force constants is lost.

To demonstrate our method we present, in the last three columns of Table I, the results of our analysis of the $X\,^1\Sigma_g^+$ ground state of Ca_2.[10] For $p = 5$ or $p = 6$, the calculated e_n do not form a monotonically decreasing set, while for $p = 7$, they do. It is this last set that we choose as our representation of the potential for this case. Three points need to be made. First, our prediction of the binding energy, while somewhat

TABLE I. Comparison of Thakkar coefficients and binding energy predictions for the $X\,^2\Sigma_g^+$ ground state of Ca_2.

	Standard analysis[b]	Our method		
R_e(Å)	4.278 5227			
p	3.556 88	5	6	7
e_0	1812.74	918.2	637.6	468.5
e_1	0	0.288 7	0.4072	0.4919
e_2	−0.255 18	0.011 87	0.1402	0.2373
e_3	−0.395 06	0.244 6	0.2132	0.2306
e_4	0.435 95	−0.050 58	0.0789	0.1455
e_5	1.061 3	0.218 7	0.1388	0.1436
e_6	−1.143 7	0.110 7	0.1244	0.1326
D_e(fit)	1274.9 cm^{-1}	1373.2	1172.9	986.3
D_e(exp)[a]	1095.0(5) cm^{-1}	1095.0(5)	1095.0(5)	1095.0(5)

[a] W. J. Balfour and R. F. Whitlock, Can. J. Phys. **53**, 472 (1975).
[b] Reference 7.

low, is closer to the experimental value than the one obtained from a standard analysis. Our prediction for D_e^T also does not have the extreme sensitivity to the value of the last coefficient that the results of the usual analysis show. Second, our method predicts a long-range behavior to the potential varying as R^{-7}, close to the R^{-6} behavior one would expect for this molecule. This is in contrast to the $R^{-3.56}$ LR behavior obtained from the usual choice of p. Third, our method of choosing p forces the $[e_n(p)]$ to be monotonically decreasing as n increases. This evidently leads to better asymptotic properties, within the range of obtainable $e_n(p)$, than the set of $e_n(p)$ displayed in the second column of Table I.

RESULTS AND DISCUSSION

We present in Table II the results of our fits to spectroscopic data for a number of van der Waals molecules. These molecules should display a long-range potential varying as R^{-n} with n an integer. The method yields a prediction for both the long-range exponent and for the binding energy D_e. As our main goal has been to devise an approach which yields good estimates of the binding energy D_e, we consider comparisons of our predicted values for D_e with experimental ones to be the principal measure of the success of our method. Case by case comparison of the two quantities, as given in Table II, reveals an overall good agreement between experimental and predicted values for D_e. The rms deviation of the predicted from experimental values is a respectable 13.1%; for the ground state fits alone, it is 6.9%.

A second measure of the success of our method is the degree to which the predicted LR exponent p agrees with the theoretically expected one (listed as n in Table II). The results are particularly satisfying on this point, with p being within one unit, in every case except XeF, from the expected value for n. For example, NaAr should have a LR interaction of the form R^{-6} for both the $X\,^2\Sigma^+_{1/2}$ and $A\,^2\Pi_{3/2}$ states; this is precisely what we obtain with $p=6$. The $BeAr^+$ molecule should have a LR potential R^{-4} arising from the ion-induced dipolar interaction. For the $X\,^2\Sigma^+$ ground state, we obtain $p=5$; while for the $A\,^2\Pi$ excited state, $p=4$. For XeF we obtain a LR behavior R^{-8} instead of the expected R^{-6} form. We have no concrete explanation for this effect, but speculate that it could be due to a change in bonding in XeF at intermediate R or simply to a failure in the method.

For comparison purposes, we also present in Table II, values for D_e obtained by two other methods. In the first, a formula presented by Goble and Winn,[8] $D_e=(9B_e^3/\alpha_e^2)[n^2/(n+1)^2]$, predicts a value for D_e from minimal spectroscopic data and an assumed LR exponent. In this expression B_e and α_e have their usual spectroscopic meanings and n is the expected LR exponent. Overall, our results are better than the predictions of this expression; for ground states alone, they are comparable to ours. It should be pointed out that the method makes systematic use of all the spectroscopic data available, and predicts p as well as D_e. The expression given above, while useful in that it uses minimal spectroscopic data and is quite accurate for ground state, is a suggested form, based on physical arguments, for the sum of $e_n(p)$ as in Eq. (5).

The last column in Table II contains the result for D_e obtained from a usual Thakkar analysis (where $p=-a_1-1$). It is seen that for some cases this approach yields a more accurate prediction for D_e, while for others it is considerably less accurate. Our reservations about the usual choice of p have already been discussed.

Most chemically bound species do not display a LR behavior R^{-p} that dominates a significant portion of the

TABLE II. Comparison of predictions of the binding energies D_e of several van der Waals diatomic molecules. All binding energies are in cm^{-1}.

		n	p	D_e(fit)	D_e(exp.)	D_e(Goble–Winn)[a]	D_e(Thakkar)
LiHe	$3d\,^2\Delta$	6	5	548.4	>471[b]	479	
NaNe	$A\,^2\Pi_{3/2}$	6	6	113.2	145(5)[c]	110.2	149.7[j]
NaAr	$X\,^2\Sigma^+_{1/2}$	6	6	42.4	41.7[d]	44.4	41.7[j]
	$A\,^2\Pi_{3/2}$	6	6	492.1	548[e]	373.6	519.4[j]
	$A\,^2\Pi_{1/2}$	6	6	460.5		373.6	572.2[j]
$BeAr^+$	$X\,^2\Sigma^+$	4	5	4192.6	4112[f]	4011	4536[k]
	$A\,^2\Pi$	4	4	13883	13656[f]	16701	
Mg_2	$X\,^1\Sigma^+_g$	6	6	382.3	424(5)[g]	371.5	528.7[l]
	$A\,^1\Sigma^+_u$	3	3	10821	9311(5)[g]	9470	
Ca_2	$X\,^1\Sigma^+_g$	6	7	986.3	1095[h]	1333	1274.9[l]
XeF	$X\,^2\Sigma$	6	8	1246.7	1175[i]	1147	

[a] References 7 and 8.
[b] A value of 510 cm^{-1} has been calculated by J. Pascale, Phys. Rev. A (to be published).
[c] W. P. Lapatovich, R. Ahmad-Bitar, P. E. Moskowitz, I. Renhorn, R. Gottscho, and D. E. Pritchard, J. Chem. Phys. **73**, 5419 (1980).
[d] G. Aepfelbach, A. Nunnemann, and D. Zimmermann, Chem. Phys. Lett. **96**, 311 (1983).
[e] R. Duren and W. Gröger, Chem. Phys. Lett. **61**, 6 (1979).
[f] K. V. Subbaram, J. A. Coxon, and W. E. Jones, Can. J. Phys. **54**, 1535 (1976).
[g] W. J. Balfour and A. E. Douglas, Can. J. Phys. **48**, 901 (1970).
[h] W. J. Balfour and R. F. Whitlock, Can. J. Phys. **53**, 472 (1975); Ref. 10.
[i] P. C. Tellinghuisen, J. Tellinghuisen, J. A. Coxon, J. E. Velazco, and D. W. Setser, J. Chem. Phys. **68**, 5187 (1978).
[j] J. H. Goble and J. S. Winn, J. Chem. Phys. **70**, 2051 (1979).
[k] Reference 7.
[l] Reference 7.

TABLE III. Comparison of predictions of the binding energies D_e of several strongly bound diatomics. All energies are in cm^{-1}. The quantities labeled (C) for O_2^- are calculated values for D_e.

		n	p	D_e(fit)	D_e(exp.)	D_e(Goble–Winn)
O_2^-	$X\,^2\Pi_g$	3	4	29078	33 530[a]	32464
	$A\,^2\Pi_u$		5	5841	(C) 6 092[a]	
	$a\,^4\Sigma_u^-$		4	11699	(C) 13 474[a]	
	$^2\Sigma_u^-$		5	5702	(C) 3 227[a]	
Li_2	$X\,^1\Sigma_g^+$	6	3	13323	8 541[b]	40318
	$A\,^1\Sigma_u^+$	3	2	16475	9 451[b]	20743
Na_2	$X\,^1\Sigma_g^+$	6	3	11218	5 988[c]	32425
I_2	$X\,^1\Sigma_g^+$	6	4	24455	12 547[d]	27025

[a] G. Das, A. C. Wahl, W. T. Zemke, and W. C. Stwalley, J. Chem. Phys. **68**, 4252 (1978).
[b] P. Kusch and M. M. Hessel, J. Chem. Phys. **67**, 586 (1977).
[c] P. Kusch and M. M. Hessel, J. Chem. Phys. **68**, 2591 (1978).
[d] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

attractive interaction. Generally, we then do not expect our method to yield good estimates of D_e for these cases. These expectations are confirmed by the results displayed in Table III, where both the prediction for p and for the binding energy fail to reproduce most of the experimental data. The results for the exceptional case of O_2^- are probably fortuitous. The failure stems directly from the lack of dominance of D_e by a LR power law potential; a situation that should prevail for our method to yield reliable results.

In summary, we have presented an alternative method of application of the generalized Thakkar expansion to the inversion of spectroscopic data. The method is generally applicable to those diatomic molecules in which a significant part of the attractive interaction has the form R^{-p}. It makes systematic use of all available data and yields good estimates for the long-range exponent p and for the dissociation energy D_e of a variety of van der Waals molecules.

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APPENDIX: EXISTENCE OF INTEGER p SUCH THAT $e_1 > e_2 > e_3 \cdots$

It is natural to ask if such an integer p can always be found so that the resulting Thakkar sequence $\{e_n\}$ is monotonically decreasing. One can readily see in fact that such a p always will exist. Indeed, from Ref. 5, we have the following connection between the Thakkar and Dunham coefficients:

$$e_0 = a_0/p^2, \tag{A1}$$

$$e_1 = 1 + (a_1 + 1)/p, \tag{A2}$$

$$e_2 = 11/12 + 3(a_1 + 1)/2p + (a_2 + 3a_1/2 + 7/12)/p^2, \tag{A3}$$

$$e_3 = 1/3 + 7(a_1 + 1)/4p + 2(a_2 + 3a_1/2 + 7/12)/p^2 + (a_3 + 2a_2 + 5a_1/4 + 1/4)/p^3, \tag{A4}$$

$$e_4 = -22/45 + 5(-\tfrac{1}{2} + 3(a_1 + 1))/p + 47(a_2 + 3a_1/2 + 7/12)/60p^2 + 5(a_3 + 2a_2 + 5a_1/4 + 1/4)/2p^3 + (a_4 + 5a_3/2 + 23a_2/6 + 3a_1/4 + 31/360)/p^4. \tag{A5}$$

Since $\alpha_e = -6B_e^2(1 + a_1)/\omega_e$ is typically positive, $(a_1 + 1) < 0$. Now for $e_1 > e_2$ we require

$$\frac{1}{12} > \frac{(a_1 + 1)}{2p} + \frac{(a_2 + 3a_1/2 + 7/12)}{p^2} \tag{A6}$$

with the first term on the right-hand side of Eq. (A6) negative. Thus this inequality is satisfied, even if the second term on the right-hand side of Eq. (A6) is positive, by choosing p sufficiently large. Similarly, $e_2 > e_3$ requires

$$\frac{7}{12} > \frac{(a_1 + 1)}{4p} + \frac{(a_2 + 3a_1/2 + 7/12)}{p^2} + \frac{(a_3 + 2a_2 + 5a_1/4 + 1/4)}{p^3}. \tag{A7}$$

This can always be satisfied providing p is chosen sufficiently large, since the new term in the inequality $e_n > e_{n+1}$ is of $O(p^{-n-1})$—cf. Eqs. (A6) and (A7). Since these inequalities place a lower bound on p, we can choose p to be an integer.

There is an unimportant upper bound on p. This arises from the requirement that $e_0 > e_1$. That is, from

$$a_0 > p[p + (a_1 + 1)].$$

This is typically only a very mild restriction on p since $a_0 \gg 1$ and $a_1 + 1 < 0$.

[1] A. L. G. Rees, Proc. Phys. Soc. **59**, 998 (1947).
[2] R. J. LeRoy, in *Molecular Spectroscopy* (The Chemical Society, Burlington House, London, 1973), Vol. 1.
[3] Derek Steele, Ellis R. Lippincott, and Joseph T. Vanderslice, Rev. Mod. Phys. **34**, 239 (1962).
[4] The expansion is a generalization of that presented in G. Simons, R. G. Parr, and J. M. Finlan, J. Chem. Phys. **59**, 3229 (1973).
[5] A. J. Thakkar, J. Chem. Phys. **62**, 1693 (1975).
[6] J. L. Dunham, Phys. Rev. **41**, 713 (1932).
[7] J. H. Goble, D. C. Hartman, and J. S. Winn, J. Chem. Phys. **67**, 4206 (1977); J. H. Goble and J. S. Winn, Chem. Phys. Lett. **77**, 168 (1981).
[8] J. H. Goble and J. S. Winn, J. Chem. Phys. **70**, 2058 (1979).
[9] K. D. Jordan, J. L. Kinsey, and R. Silbey, J. Chem. Phys. **61**, 911 (1974).
[10] Data from C. R. Vidal, J. Chem. Phys. **72**, 1864 (1980).