Brief Reports

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Number of quasibound levels behind a rotational barrier

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The number of quasibound or rotationally predissociating levels of diatomic molecules is investigated using a long-range approximation of the difference between the Jeffreys-Wentzel-Kramers-Brillouin estimates of the vibrational quantum numbers at the maximum of the rotational barrier and at the dissociation limit. It is found that for a fixed J the expected number of quasibound levels is approximately $J/20$, essentially independent of the magnitude and form of the potential and independent of the mass of the nuclei.

The effective interatomic potential for a rotating diatomic molecule, $U_J(R)$, is typically represented at large R by adding the rotational kinetic energy to a single-term multipole expansion, giving an expression of the form

$$U_J(R) \rightarrow \hbar^2 J(J+1)/2\mu R^2 - C_n/R^n . \tag{1}$$

Such a potential has a maximum value of

$$E_b \simeq [\hbar^2 J(J+1)/\mu]^{n/(n-2)}(nC_n)^{-2/(n-2)}(\tfrac{1}{2}-1/n) , \tag{2}$$

at

$$R_b \simeq \left[\frac{n\mu C_n}{\hbar^2 J(J+1)} \right]^{1/(n-2)} , \tag{3}$$

derived from the condition $U_J'(R_b)=0$. We are interested in estimating the number of quasibound vibrational levels that can exist behind this barrier. To do this we follow Stogryn and Hirschfelder[1] and Dickinson and Bernstein[2] and construct the Jeffreys-Wentzel-Kramers-Brillouin (JWKB) estimate for the vibrational quantum number v_b at the barrier maximum $E = E_b$, and compare it with the vibrational quantum number v_0 at the dissociation limit $E = 0$. Suppose that $R_1(E_b)$ and $R_2(E_b) = R_b$ are the left- and right-hand turning points for $E = E_b$, as shown in Fig. 1(a); then,

$$v_b + \tfrac{1}{2} = \alpha \int_{R_1(E_b)}^{R_2(E_b)} [E_b - U_J(R)]^{1/2} dR , \tag{4}$$

where $\alpha = \sqrt{(2\mu)}/(\pi\hbar)$. Similarly, if $R_1(0)$ and $R_2(0) \simeq R_0$ are the left- and right-hand turning points for $E = 0$, we have

$$v_0 + \tfrac{1}{2} = \alpha \int_{R_1(0)}^{R_2(0)} [-U_J(R)]^{1/2} dR . \tag{5}$$

Thus

$$
\begin{aligned}
v_b - v_0 = &\alpha \int_{R_1(E_b)}^{R_1(0)} [E_b - U_J(R)]^{1/2} dR \\
&+ \alpha \int_{R_1(0)}^{R_2(0)} \{ [E_b - U_J(R)]^{1/2} \\
&\qquad\qquad - [-U_J(R)]^{1/2} \} dR \\
&+ \alpha \int_{R_2(0)}^{R_2(E_b)} [E_b - U_J(R)]^{1/2} dR .
\end{aligned}
\tag{6}
$$

Following the approach of LeRoy and Bernstein,[3] we plan to ignore the first term [supposing that $R_1(E_b)-R_1(0)$ is small and that the repulsive wall is steep] and to replace $U_J(R)$ by its asymptotic expansion. This gives

$$
\begin{aligned}
v_b - v_0 \simeq &\beta \int_0^1 \{ [1 - U_J(R)/E_b]^{1/2} \\
&\qquad + [-U_J(R)/E_b]^{1/2} \}^{-1} dy \\
&+ \beta \int_1^{R_b/R_0} [1 - U_J(R)/E_b]^{1/2} dy ,
\end{aligned}
\tag{7}
$$

where we have substituted $\beta = \alpha R_0 \sqrt{E_b}$ and $y = R/R_0$. See Fig. 1(b) for a comparison of the exact [Eq. (6)] and long-range approximation [Eq. (7)] to the JWKB difference integrand. Deriving

$$R_0 \simeq \left[\frac{2\mu C_n}{\hbar^2 J(J+1)} \right]^{1/(n-2)} \tag{8}$$

from the condition $U_J(R_0)=0$, we are ready to perform a number of back substitutions.

The remarkable result of these substitutions is that the molecular parameters μ and C_n disappear entirely, and
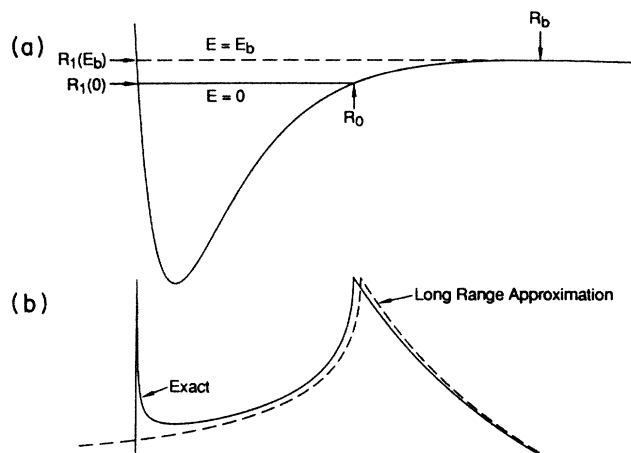
FIG. 1. (a) Upper curve: Effective potential $U_J(R)$ based on a Leonard-Jones (12,6) form. (b) Lower curves: JWKB difference integrands for the exact potential and for the long-range approximation.

TABLE I. Numerical values for the integral I_n.

n	Present	Ref. 2
3	0.0451	
4	0.0498	0.0498
5	0.0498	
6	0.0482	0.0482
7	0.0462	
8	0.0441	0.044
9	0.0420	
10	0.0401	

only the dependencies on n and J remain. We first note that $R_b/R_0 = (n/2)^{1/(n-2)} \equiv \rho_n$, then we evaluate $\beta = [J(J+1)/\gamma_n]^{1/2}/\pi$, where

$$\gamma_n = \frac{(n/2)^{n/(n-2)}}{(n/2 - 1)} , \qquad (9)$$

and further observe that $-U_J(R)/E_b = \gamma_n(y^{-n} - y^{-2})$. Thus we have

$$v_b - v_0 \simeq [J(J+1)]^{1/2} I_n , \qquad (10)$$

where

$$I_n = \frac{1}{\pi\sqrt{\gamma_n}} \left[\int_0^1 \{[1 + \gamma_n(y^{-n} - y^{-2})]^{1/2} \right.$$

$$+ [\gamma_n(y^{-n} - y^{-2})]^{1/2}\}^{-1} dy$$

$$\left. + \int_1^{\rho_n} [1 + \gamma_n(y^{-n} - y^{-2})]^{1/2} dy \right] . \qquad (11)$$

We have just shown that the number of quasibound levels does not depend on μ and C_n.

An even more surprising result is obtained when we evaluate the integral I_n. Integrating numerically we find the results given in Table I, and we conclude that the number of quasibound vibrational levels is effectively independent of n as well. Also included in Table I are the numbers derived by Dickinson and Bernstein[2] for $n = 4$, 6, and 8. They considered potentials for which the JWKB integrals for v_b and v_0 could be evaluated explicitly in terms of elliptic integrals and extracted the leading term in J of the difference between them. They noticed the near independence on n, but their formulation did not make clear that the expected number of quasibound levels for low J,

$$N_{QB}(J) = v_b - v_0 = 0.048 \pm 0.02[J(J+1)]^{1/2}$$

$$\simeq J/20 , \qquad (12)$$

is entirely independent of the molecule under consideration.

To assess the applicability of the expressions derived above, we have examined the published compilations of quasibound levels in which it is claimed that all the quasibound levels have been calculated. The formula for $N_{QB}(J)$ above indicates the average number of quasibound levels expected. For any specific J, we expect to find at least $J/20 - 1$ and at most $J/20 + 1$ levels. To evaluate whether the number of levels found matches our expectation we count all the levels expected for angular momenta up to the specific value of J,

$$T_{QB}(J) = \sum_{L=0}^{J} N_{QB}(L) \simeq J(J+2)/40 . \qquad (13)$$

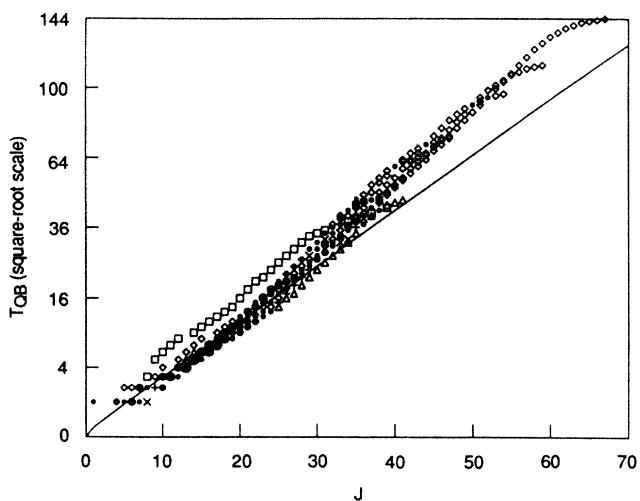Figure 2 shows a graphical comparison of the numbers

FIG. 2. Graphical comparison of expected number of quasibound levels with the numbers found in exact calculations. $\times$'s, HeH$^+$ (Ref. 4); $+$'s, CH$^+$ (Ref. 5); diamonds, H_2, HD, D_2 (Ref. 6) and HT, DT, T_2 (Ref. 7); squares, HgH (Refs. 8 and 9); triangles, H_2^+ (Refs. 10 and 11); filled circles, more than one superimposed symbol.

TABLE II. Numbers of quasibound levels in ranges of J.

	J_{max}	T_{QB} obs	T_{QB} calc	N_{QB} in ranges of J's, $T_{QB}(J)-T_{QB}(J-10)$						
				0–9	10–19	20–29	30–39	40–49	50–59	60–69
$^3He^1H^+$ [a]	26	20	19	2	8	10				
$^4He^1H^+$ [a]	27	21	20	2	7	14				
$^3He^1H^+$ [a]	34	32	31	1	8	14	7			
CH^+ [b]	36	37	34	2	6	15	14			
$^4He^2H^+$ [a]	36	39	34	2	8	17	12			
H_2 [c]	38	47	38	2	8	19	18			
HgH [d]	39	43	40	5	9	10	10			
H_2^+ [e]	41	46	44	2	6	12	23	2		
HD [c]	44	65	51	3	8	18	19	7		
HT [f]	47	73	58	2	8	16	30	17		
D_2 [c]	54	96	76	2	7	15	17	36	8	
DT [f]	59	113	90	1	8	15	25	36	28	
T_2 [f]	67	144	116	1	7	16	24	34	45	17
Eq. (13)				2.5	7.5	12.5	17.5	22.5	27.5	32.5

[a] Reference 4.
[b] Reference 5.
[c] Reference 6.
[d] References 8 and 9.
[e] References 10 and 11.
[f] Reference 7.

of quasibound levels found in exact calculations from the literature with the above simple formula (we have used a square-root scale on the y axis to make the low J values more discernible). For low J (say <30), the present theory is clearly consistent with the exact results. The only exceptional case is HgH, for which the potential is known to have an abrupt change of form at $R \simeq 4$ Å (Ref. 12) and thus cannot be represented by a single long-range multipole term. For higher values of J, the present theory consistently underestimates the number of quasibound levels, because of the increasing contribution of the left-hand turning points to the JWKB difference integral; however, the exact calculations continue to exhibit a common dependence on J.

Table II shows numerical summaries of these same comparisons. The levels have been grouped in ranges of ten values of J. Again, we see that essentially perfect agreement for low J and rather good agreement even for the total number of quasibound levels up to the highest J for which quasibound levels are supported by the potential.

[1] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. **31**, 1531 (1959).
[2] A. S. Dickinson and R. B. Bernstein, Mol. Phys. **18**, 305 (1970).
[3] R. J. LeRoy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970).
[4] R. I. Price, Chem. Phys. **31**, 309 (1978).
[5] H. Helm, P. C. Cosby, M. M. Graff, and J. T. Moseley, Phys. Rev. A **25**, 304 (1982).
[6] R. J. LeRoy, J. Chem. Phys. **54**, 5433 (1971); University of Wisconsin Theoretical Chemistry Institute Report No. WIS-TCI-387, 1971 (unpublished).
[7] C. Schwartz and R. J. LeRoy, J. Mol. Spec. **121**, 420 (1987); R.
J. LeRoy and C. Schwartz, University of Waterloo Chemical Physics Research Report No. CP-301R (revised 2nd printing, 1987) (unpublished).
[8] W. C. Stwalley, A. Niehaus, and D. R. Herschbach, J. Chem. Phys. **63**, 3081 (1975).
[9] M. Hehenberger, P. Froelich, and E. Brändas, J. Chem. Phys. **65**, 4571 (1976).
[10] M. Kuriyan and H. O. Pritchard, Can. J. Phys. **55**, 3420 (1977).
[11] J. P. Davis and W. R. Thorson, Can. J. Phys. **56**, 996 (1978).
[12] W. C. Stwalley, J. Chem. Phys. **63**, 3062 (1975).