

5.73 Lecture #8

Rydberg Klein Rees

8 - 1

Last time: WKB quantization condition for bound eigenstates of almost general $V(x)$ — Connection into bound region from left and right

$$\int_{x_-(E)}^{x_+(E)} p_E(x') dx' = \frac{h}{2} (n + 1/2)$$

$$p_E(x) = [2m(E - V(x))]^{1/2}$$

E_n without ψ_n !

But where do we get $V(x)$?

Certainly not from femtochemistry!

From FREQUENCY DOMAIN SPECTROSCOPY

$E_{v,J} \rightarrow V(x)$

timing of w.p. as it moves on $V(x)$

RKR method

Next time: Numerical Integration of 1-D Schr. Eq. — see handouts

Then begin working toward matrix picture

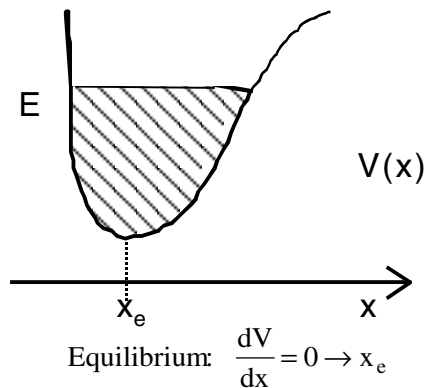
Need background in Ch.2 of CTDL

pages 94-121 soon, pages 121-144 by next week

Postulates and theorems not to be covered except as needed for solving problems.

Today: $E_{v,J} \rightarrow$ spectroscopic notation

$A(E, J) =$



$$\frac{\partial A}{\partial E}, \frac{\partial A}{\partial J} \rightarrow x_+(E) - x_-(E) \text{ and } \frac{1}{x_+(E)} - \frac{1}{x_-(E)}$$

WKB QC applied to $\frac{\partial A}{\partial E}, \frac{\partial A}{\partial J} \leftarrow G(v), B(v)$ used to determine $x_{\pm}(E)$.

Long Range Theory: Ultra Cold Collisions: Atom in Molecule

Someday you will discover that the energy levels of a diatomic molecule are given by

$$E_{evJ} / hc = T_e + \underbrace{G(v)}_{\text{vibration}} + \underbrace{F_v(J)}_{\text{rotation}} \quad \text{cm}^{-1}$$

$$= v_e + \left[Y_{00} + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots \right]$$

$$+ \left[\underbrace{B_e - \alpha_e(v + 1/2) + \dots}_{B(v)} \right] J(J + 1) - DJ^2(J + 1)^2$$

RKR requires only $G(v)$ and $B(v)$ to get $V_J(x)$

where $V_J(x) = U(x) + \frac{\hbar^2 J(J + 1)}{2\mu x^2}$ $x \equiv R - R_e$

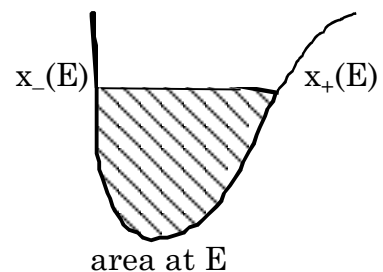
J-dependent effective potential
bare potential
centrifugal barrier (actually rotational kinetic energy)
 $\mu = \frac{m_1 m_2}{m_1 + m_2}$

We are going to derive $V_0(x)$ directly from $G(v)$, $B(v)$ data. This is the only direct spectrum to potential inversion method! WKB quantization is the basis for this.

$$\int_{x_-(E_v)}^{x_+(E_v)} p_{E_v}(x') dx' = (h/2)(v + 1/2) \quad v = 0, 1, \dots \# \text{ of nodes}$$

In this equation, what we know (E_v) and what we want ($V(x)$ and x at turning points) are hopelessly mixed up. There is a trick!

$$A(E, J) \equiv \int_{x_-(E, J)}^{x_+(E, J)} \left[E \pm V_J(x') \right] dx'$$



but, still, we know neither $V_J(x)$ nor $x_{\pm}(E,J)!!$

Roadmap: 1. Show that $\frac{\partial A}{\partial E}$ and $\frac{\partial A}{\partial J}$ are numerically evaluable
 data input here \rightarrow integrals (via WKB QC) involving only $E_{v,J}$ info
 2. independently, $\frac{\partial A}{\partial E}$ and $\frac{\partial A}{\partial J}$ determine
 2 eqs. in 2 unknowns give turning points \rightarrow $[x_+(E,J) - x_-(E,J)]$ and $\left[\frac{1}{x_+(E,J)} - \frac{1}{x_-(E,J)} \right]$

Do #2 first because it is so easy

$$\frac{\partial A}{\partial E} = \frac{\partial}{\partial E} \left[\int_{x_-(E,J)}^{x_+(E,J)} \left[E - U(x') - \frac{\hbar^2 J(J+1)}{2\mu x'^2} \right] dx' \right]$$

$$= \int_{x_-(E,J)}^{x_+(E,J)} 1 dx' + \underbrace{0 + 0}_{\substack{\text{Contributions from } \frac{\partial x_{\pm}(E,J)}{\partial E} \\ \text{are zero because integrand is 0} \\ \text{at turning points}}}$$

$$\boxed{\frac{\partial A}{\partial E} = x_+(E,J) - x_-(E,J)} \quad !$$

$$\frac{\partial A}{\partial J} = \frac{\partial}{\partial J} \left[\int_{x_-(E,J)}^{x_+(E,J)} \left[E - U(x') - \frac{\hbar^2 J(J+1)}{2\mu x'^2} \right] dx' \right]$$

$$= -\frac{\hbar^2}{2\mu} \int_{x_-(E,J)}^{x_+(E,J)} \frac{2J+1}{x'^2} dx' + \underbrace{0 + 0}_{\text{integrand} = 0 \text{ at } x_{\pm}}$$

$$\boxed{\frac{\partial A}{\partial J} = +\frac{\hbar^2(2J+1)}{2\mu} \left[\frac{1}{x_+(E,J)} - \frac{1}{x_-(E,J)} \right]}$$

So, if we can evaluate these derivatives from $E_{v,J}$ data, we have $V_J(x)!$

some clever manipulations to put $A(E, J)$ into convenient form
 (see nonlecture notes on pages 8-5,6,7)

$$A(E, J) = \int_{x_-(E, J)}^{x_+(E, J)} [E \pm V_J(x')] dx'$$

$$A(E, J) = 2 \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \int_{\underbrace{v(E_{\min}, J)}_{\text{data}}}^{v(E, J)} \left[E \pm \underbrace{E'_{vJ}}_{\text{data}} \right]^{1/2} dv$$

skipped steps are shown
 on pages 8-5, 6, 7.

this integral could be evaluated at any E , but we really only want $\frac{\partial A}{\partial E}$ and $\frac{\partial A}{\partial J}$. Evaluate these derivatives at $J = 0$.

$$\frac{\partial A}{\partial E} = 2 \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \left(\frac{1}{2} \right) \int_{v(E_{\min}, J)}^{v(E, J)} [E - E'_{vJ}]^{-1/2} dv + 0 + 0$$

lower limit independent of E

integrand = 0 at upper limit

$$v(E_{\min}, J) = -\frac{1}{2} - \frac{Y_{00}}{\omega_e}$$

defined so that $G(v_{\min}) = 0$

$$\left[\begin{array}{l} G(v) = Y_{00} + \omega_e(v + 1/2) \\ 0 = G(v_{\min}) = Y_{00} + \omega_e(v_{\min} + 1/2) \\ -\frac{Y_{00}}{\omega_e} = v_{\min} + 1/2 \\ v_{\min} = -\frac{Y_{00}}{\omega_e} - \frac{1}{2} \end{array} \right]$$

[v_{\min} is slightly different from $-1/2$]

for $J = 0$ $E'_{v, J} = G(v)$

$$\frac{\partial A}{\partial E} = \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \int_{-1/2 - Y_{00}/\omega_e}^{v(E)} [E - G(v)]^{-1/2} dv \equiv 2f(E)$$

evaluate this integral numerically at any E .

[Singularity at upper limit fixed by change of variable: Zeleznik JCP 42, 2836 (1965).]

$$\left. \frac{\partial A}{\partial J} \right|_{J=0} = \left(\frac{2\hbar^2}{\mu} \right) \int_{-1/2 - Y_{00}/\omega_e}^{v(E)} [E - G(v)]^{-1/2} \frac{\partial E}{\partial J} dv + 0 + 0$$

$$E = B_J J(J+1)$$

$$\frac{\partial E}{\partial J} = B_v(2J+1) \quad \left. \frac{\partial E}{\partial J} \right|_{J=0} = B_v$$

$$\therefore \left. \frac{\partial A}{\partial J} \right|_{J=0} = \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \int_{-1/2 - Y_{00}/\omega_e}^{v(E)} [E - G(v)]^{-1/2} B_v dv \equiv - \left(\frac{\hbar^2}{2\mu} \right) 2g(E)$$

(again, a nonfatal singularity at upper limit)

$f(E)$ and $g(E)$ are “Klein action integrals” which are jointly determined by empirical $G(v)$ and $B(v)$ functions.

Nonlecture derivation of this useful form of

$$A(E, J) = 2 \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \int_{v(E_{\min}, J)}^{v(E, J)} [E - E'_{vJ}]^{1/2} dv$$

Begin here: $A(E, J) = \int_{x_-(E, J)}^{x_+(E, J)} [E - V_J(x')] dx'$

integral identity $b - a = \frac{2}{\pi} \int_a^b \left(\frac{x - a}{b - x} \right)^{1/2} dx$

let $b = E$

$a = V_J(x)$

$x = E'_{vJ}$

so that $\left(\frac{x - a}{b - x} \right) = \frac{E_{vJ} - V_J(x)}{E - E_{vJ}}$

$$\therefore A(E, J) = \int_{x_-(E, J)}^{x_+(E, J)} [b - a] dx'$$

Now insert the integral identity

$$A(E, J) = \int_{x_-(E, J)}^{x_+(E, J)} \left(\frac{2}{\pi} \int_a^b \left[\frac{x-a}{b-x} \right]^{1/2} dx \right) dx' \quad \text{put in values of } a, b, \text{ and } x$$

$$= \int_{x_-(E, J)}^{x_+(E, J)} \left(\frac{2}{\pi} \int_{V_J(x)}^E \left[\frac{E'_{vJ} - V_J(x')}{E - E'_{vJ}} \right]^{1/2} dE'_{vJ} \right) dx'$$

reverse order of integration and recognize WKB QC in disguise

$$= \frac{2}{\pi} \int_{V_J(x)}^E \left(\int_{x_-(E, J)}^{x_+(E, J)} \left[\frac{E'_{vJ} - V_J(x')}{E - E'_{vJ}} \right]^{1/2} dx' \right) dE'_{vJ}$$

numerator of dx' integral is QC — insert QC and then integrate by parts.
denominator is independent of x' , so insert QC

$$\int_{x_-(E, J)}^{x_+(E, J)} [E' - V(x')]^{1/2} dx' = (2\mu)^{-1/2} \int_{x_-}^{x_+} p(x') dx'$$

$$= (2\mu)^{-1/2} \frac{h}{2} (v + 1/2)$$

$$\therefore A(E, J) = \left(\frac{2}{\pi} \right) (2\mu)^{-1/2} \frac{h}{2} \int_{E_{\min}}^E \left[\frac{v(E', J) + 1/2}{(E - E'_{vJ})^{1/2}} \right] dE'_{vJ} \quad **$$

** integrate by parts

$$f' = (E - E'_{vJ})^{-1/2}$$

$$f = -2(E - E'_{vJ})^{1/2} \quad (\text{not a typo because variable is } E'_{vJ} \text{ not } E)$$

$$g = [v(E'_{vJ}, J) + 1/2]$$

$$g' = \frac{dv}{dE'}, \quad \text{which is known from } E_{vJ}$$

$$A(E, J) = \underbrace{fg}_{=0 \text{ at both limits}}^{E'=E}_{E'=E_{\min}} + \left(\frac{2h^2}{\mu} \right)^{1/2} \int_{E_{\min}}^E 2(E - E')^{1/2} \frac{dv}{dE'} dE'$$

(caution: f and g here are not Klein's action integrals)

** change variables from dE' to dv'

$$dv = \frac{dv}{dE'} dE'$$

limits of integration become $\int_{v(E_{\min}, J)}^{v(E, J)}$

$$\text{finished: } A(E, J) = 2 \left(\frac{2\hbar^2}{\mu} \right)^{1/2} \int_{v(E_{\min}, J)}^{v(E, J)} [E - E'_{vJ}]^{1/2} dv$$

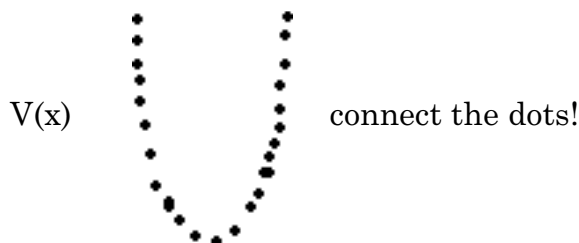
we have two independent evaluations of $f(E)$ and $g(E)$

$$\text{one leads to } x_+(E, 0) - x_-(E, 0) = 2f(E)$$

$$\frac{1}{x_+(E, 0)} - \frac{1}{x_-(E, 0)} = \pm 2g(E)$$

$$\text{pair of turning points } x_{\pm}(E, 0) = \left[f(E) / g(E) + f(E)^2 \right]^{1/2} \pm f(E) \quad \text{from quadratic formula}$$

so we get a pair of turning points at each E . Not restricted to E 's with integer v 's!



Robert LeRoy: modern, n-th generation RKR program at

<http://theochem.uwaterloo.ca/~leroy/>

Download program, instructions, and sample data.

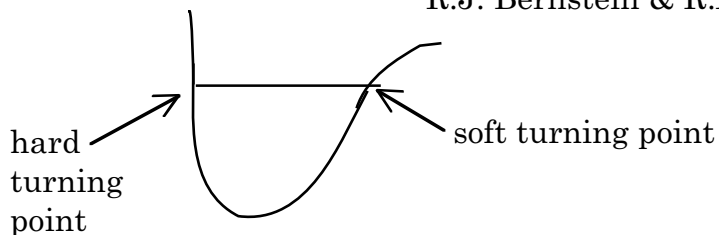
RKR does not work for polyatomic molecules because $E - V(\vec{Q})$ does not determine the multicomponent vector \vec{P}

5.73 Lecture #8

Rydberg Klein Rees

8 - 8

Long-Range Molecules $\left\{ \begin{array}{l} \text{W.C. Stwalley CPL } \underline{6}, 241 (1970) \\ \text{(weak perturbation of atomic properties)} \\ \text{R.J. Bernstein \& R.LeRoy JCP } \underline{52}, 3869 (1970) \end{array} \right.$



What does $\psi(x)$ look like at very high v ?

- * lots of nodes (v nodes)
- * *small* lobe at inner turning point. Why?
- * *large* lobe at outer turning point. Why?

Hint: Force = $-\frac{dV(x)}{dx}$

at sufficiently large v , it is certain that $\psi(x)$ is dominated by outer-most lobe and any expectation value of a function of x , such as $V(x)$, will be dominated by the outer turning point region. Since the vibrational Schrödinger equation contains $V(x)$, it is evident that E_v at high v should be determined primarily by the long range part of $V(x)$ (and insensitive to details near x_e and at the inner turning point).

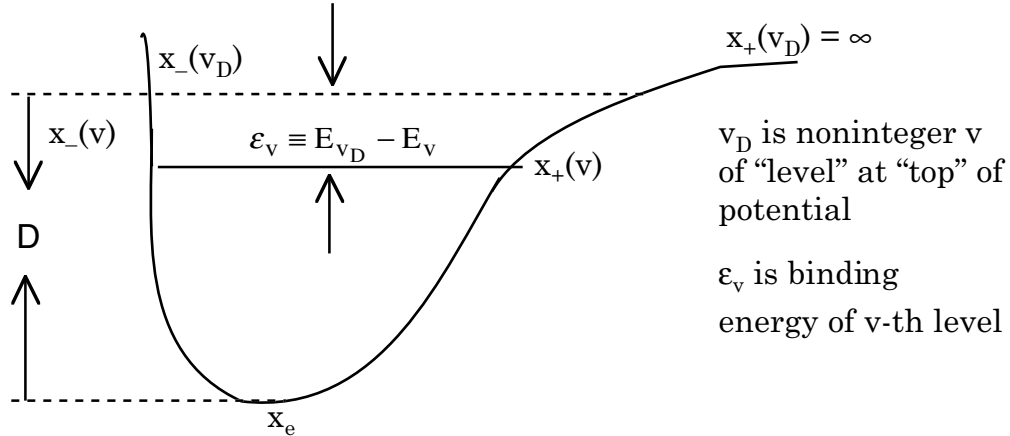
What do we know about covalent bonding?

ATOMIC ORBITAL OVERLAP IS REQUIRED!

NO OVERLAP at large x , $V(x)$ determined by properties of isolated atoms: dipole moment, polarizability — return to this later when we do perturbation theory.

It is always possible to predict the longest range term in $V(x) = C_n x^{-n}$ where the longest range term is the one with **SMALLEST** n .

Quick review of the Long-Range Theory



at $J = 0$ $V_0(x) = U(x) = -C_n x^{-n}$ at long range (large x)

$$U(\infty) = 0 \equiv E_{v_D}$$

$$U(x_e) = -D_e$$

$$x_+(v) = (-C_n/E_v)^{1/n} \quad \left[E_v = V(x_+(v)) = -C_n x_+^{-n} \right]$$

$$x_+(v_D) = \infty$$

binding energy: $\epsilon_v = E_{v_D} - E_v = C_n x_+^{-n}$

How many levels are there in potential?

$$\frac{h}{2}(v_D + 1/2) = \int_{x_-(v_D)}^{x_+(v_D)=\infty} p_D(x') dx'$$

Now we do not know v_D , C_n , or D , but we do know n and know that E_v will be primarily determined by long-range part of $V(x)$ near v_D . So, for any E_v we expect that it will be possible to derive a relationship between

$(v_D - v)$ # of levels below highest bound level

and $(E_{v_D} - E_v)$ binding energy

by some clever tricks you may discover on Problem Sets #4 and 5, we find

$$v_D - v = a_n \epsilon_v^{\frac{n-2}{2n}}$$

Tells us how to plot E_v vs. v to extrapolate to v_D and then to obtain accurate value of D_e from a linear plot near dissociation.

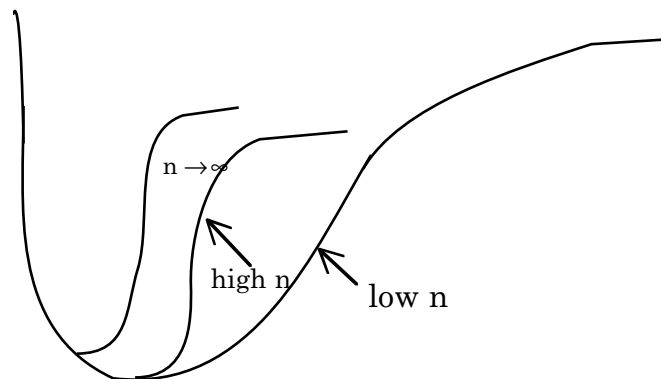
Power of longest range term in $V(x)$:

n=1 charge - charge	+,- point charges (e.g. H atom)
2 charge - dipole	—
3 charge - induced dipole	$H^+ + H$
3 dipole - dipole	$Na(^2S) + Na(^2P)$
(also transition dipoles)	—
5 dipole - induced dipole	$I(^2P_{3/2}) + I(^2P_{3/2})$
5 quadrupole - quadrupole	$Na(^2S) + Na(^2S)$
6 induced dipole - induced dipole	

not only is the limiting n known, but also C_n is known because it is calculable from a measurable property of the free atom. Many molecular states are described at long range by the same C_n 's! Ultra-cold collisions now used to determine $V(x)$ to very large x . Now best route to the properties of separated atoms!

Mostly, long-range theory has been used as a guide to extrapolation to accurate dissociation energy (relevant to ΔH_f°). Now Bose condensates. Molecule trapping.

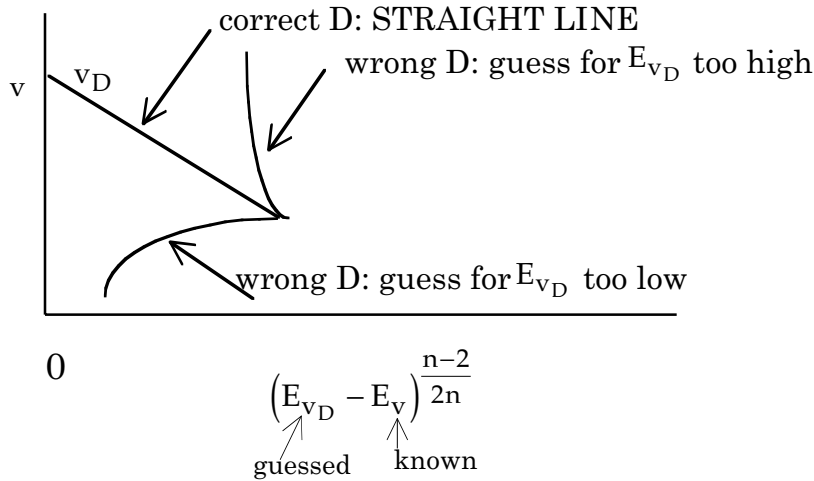
x^{-1} and x^{-2} potentials have ∞ number of bound levels. x^{-3}, x^{-5}, x^{-6} potentials have finite number, and the number of levels breaks off more abruptly as n increases.



i.e., # of bound levels

action integral affected more by wider classical Δx region than by deeper ΔE binding region because $p \propto (E - V(x))^{1/2}$

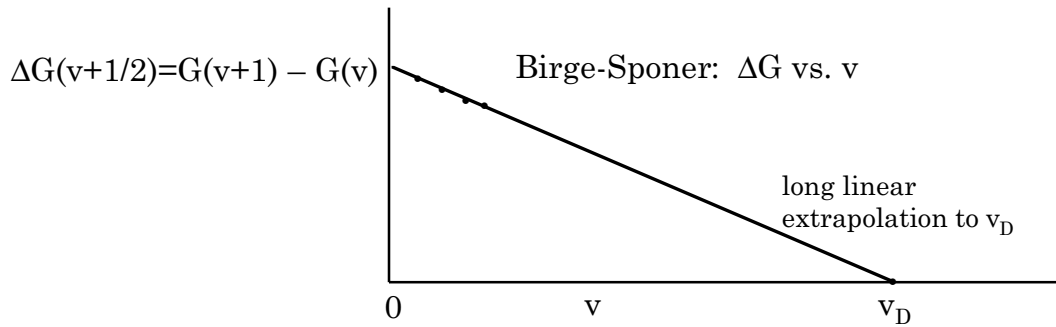
This means (equation at bottom of 8-9) that if we plot (given that we can predict n with certainty)



n	$\frac{n-2}{2n}$
3	1/6
5	3/10
6	1/3
7	5/14

it is possible to determine D and v_D very accurately

much better than Birge – Sponer plot, which is valid only for a Morse potential



for Morse $G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2$

$\Delta G(v + 1/2) = G(v + 1) - G(v) = \omega_e - \omega_e x_e (2v + 2)$ decreasing to 0 as v increases

Morse Potential

when $\Delta G(v + 1/2) = 0$, $\omega_e = \omega_e x_e (2v + 2)$

$V_0(x) = D[1 - e^{-Ax}]^2$

$v_D = \frac{\omega_e}{2\omega_e x_e} - 1$ v_D is noninteger # of bound vibrational levels

$$D = G(v_D) = \frac{1}{4} \left[\frac{\omega_e^2}{\omega_e x_e} - \omega_e x_e \right]$$

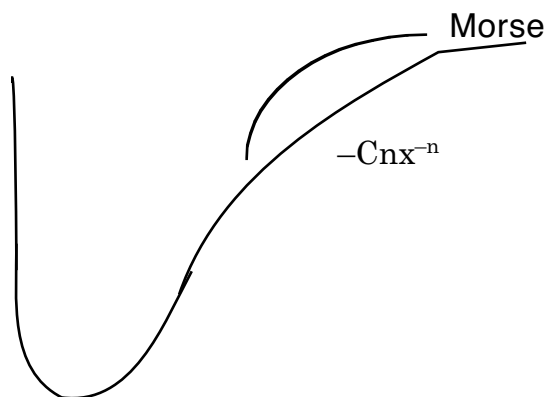
$$= (v_D + 1) \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} \approx (v_D + 1) \frac{\omega_e}{2}$$

But Morse inevitably has incorrect long-range form

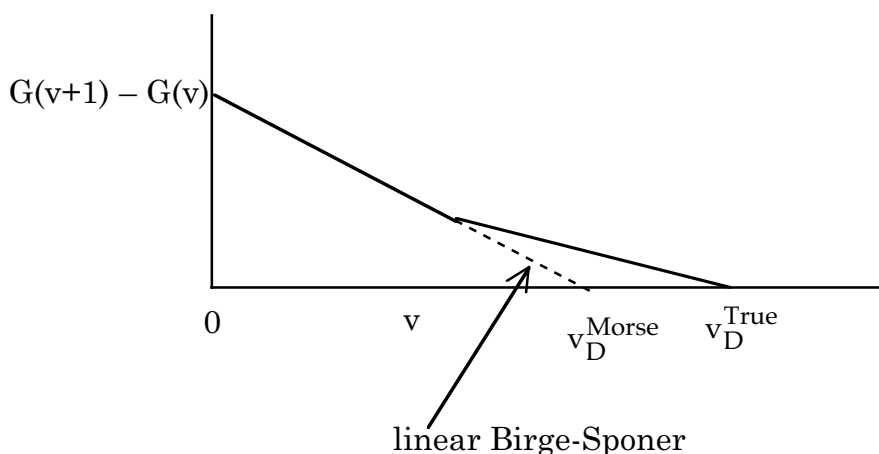
Which is longer range? Morse or $C_n x^{-n}$? Take ratio of binding energy at large x .

$$\begin{aligned} \lim_{x \rightarrow \infty} \frac{-C_n x^{-n}}{D[1 - e^{-Ax}]^2 - D} &= \lim_{x \rightarrow \infty} \frac{-C_n x^{-n}}{D e^{-2Ax} - 2D e^{-Ax}} \\ &= \lim_{x \rightarrow \infty} \frac{-C_n x^{-n} e^{2Ax}}{D - \boxed{2D e^{Ax}}} \leftarrow \text{dominant term} \\ &= \lim_{x \rightarrow \infty} \frac{C_n}{2D} x^{-n} e^{Ax} \rightarrow \infty \end{aligned}$$

This means that Morse binding energy gets small faster than $C_n x^{-n}$ for *any* n .



$G(v+1) - G(v)$ will get small faster for Morse. Plot $\Delta G(v + 1/2)$ vs. v .



Dissociation energy usually underestimated by linear Birge-Sponer extrapolation. Long-range plot of correct power of $E_{v_D} - E_v$ gives more accurate dissociation energy.