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

$$\boxed{\begin{aligned}\int_{x_-(E)}^{x_+(E)} p_E(x')dx' &= \frac{h}{2}(n+1/2)\\ p_E(x) &= [2m(E-V(x))]^{1/2}\end{aligned}}$$

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)?

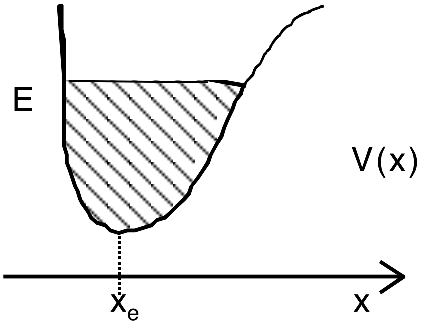
RKR method

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 : cm^{-1} units,

T electronic
G vibrational
F rotational

$A(E,J) =$



Equilibrium: $\frac{dV}{dx} = 0 \rightarrow x_e$

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

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

Long Range Theory: Ultra Cold Collisions: Atom in Molecule

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

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

$$= \nu_e + \Big[Y_{00} + \underbrace{\omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \ldots}_{G(v)}\Big]$$

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

RKR requires only <u>G(v)</u> and <u>B(v)</u> to get <u>$V_J(x)$</u>

$$\text{where } \underset{\substack{\text{J-dependent}\\ \text{effective}\\ \text{potential}}}{V_J(x)} = \underset{\substack{\text{bare}\\ \text{potential}}}{U(x)} + \underset{\substack{\text{centrifugal barrier}\\ \text{(actually rotational}\\ \text{kinetic energy)}}}{\frac{\hbar^2 J(J+1)}{2\mu x^2}} \qquad x \equiv R - R_e$$

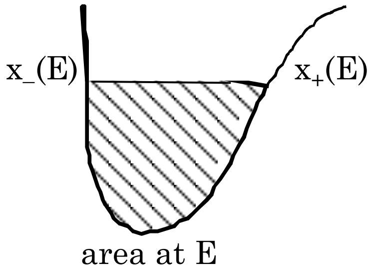
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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. It is easy to go from $V_0(x)$ to G(v) and B(v), but RKR is special.

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

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 integrals (via WKB QC) involving only $E_{v,J}$ info

data input here

2. independently, $\frac{\partial A}{\partial E}$ and $\frac{\partial A}{\partial J}$ determine $[x_+(E,J) - x_-(E,J)]$ and $\left[\frac{1}{x_+(E,J)} - \frac{1}{x_-(E,J)}\right]$

2 eqs. in 2 unknowns give turning points

Do #2 first because it is so easy

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

$$= \int_{x_-(E,J)}^{x_+(E,J)} 1dx' \qquad + \boxed{0 \quad + \quad 0}$$

contributions from $\frac{\partial x_{\pm}(E,J)}{\partial E}$ are zero because integrand is 0 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_{vJ} 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)

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

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

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.

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

integrand = 0 at upper limit

lower limit independent of E

$$\underset{\substack{\downarrow \\ \text{defined so that } G(v_{min}) = 0}}{v(E_{min},J)} = -\frac{1}{2} - \frac{Y_{00}}{\omega_e}$$

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

[v_{min} is slightly different from −1/2]

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

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

evaluate this integral numerically at any E.

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

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

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

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

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

(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

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

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

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

let $\quad b = E$

$a = V_J(x)$

$x = E'_{vJ}$

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

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

Now insert the integral identity

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

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

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

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

** integrate by parts

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

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

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

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

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

(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 $\int_{v(E_{\min},J)}^{v(E,J)}$

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

---

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

one leads to $x_+(E,0) - x_-(E,0) = 2f(E)$

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

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

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

V(x)  connect the dots!

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

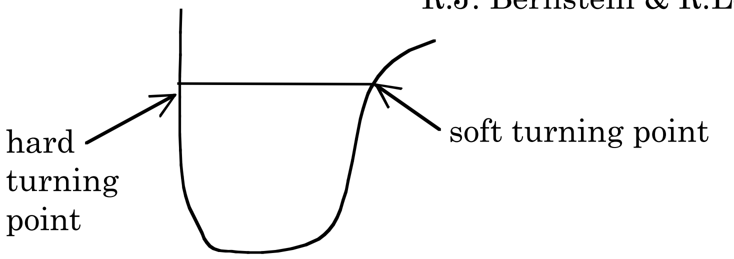
http://theochem.uwaterloo.ca/~leroy/

Download program, instructions, and sample data.

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

Long-Range Molecules

W.C. Stwalley CPL 6, 241 (1970)
(weak perturbation of atomic properties)
R.J. Bernstein & R.LeRoy JCP 52, 3869 (1970)



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?

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

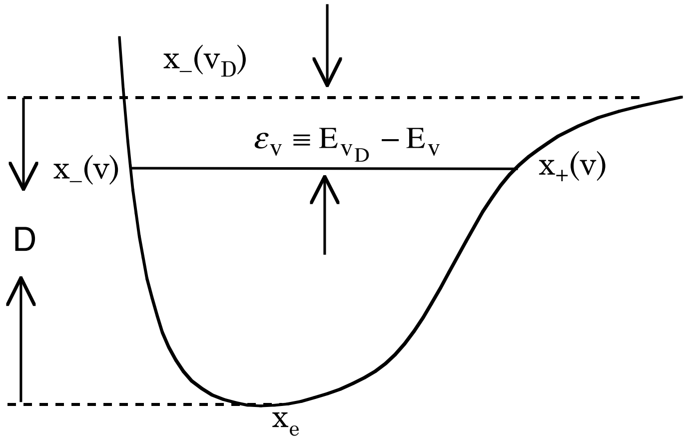
at sufficiently large v, it is certain that $\psi(x)$ is dominated by outer-most lobe and any expectation value of a function of x, such as V(x), will be dominated by the outer turning point region. Since the vibrational Schrödinger equation contains V(x), it is evident that E_v at high v should be determined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

The lobe of $\psi(x)$ we use to sample V(x) sees nearly pure atomic electronic properties.

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



$x_+(v_D) = \infty$

v_D is noninteger v of “level” at “top” of potential

ε_v is binding energy of v-th level

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

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

$$U(x_e) = -D_e$$

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

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

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

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

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

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.

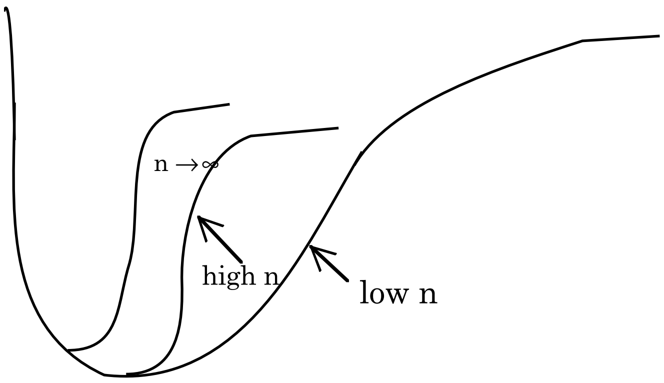
Power of longest range term in V(x):

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

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.

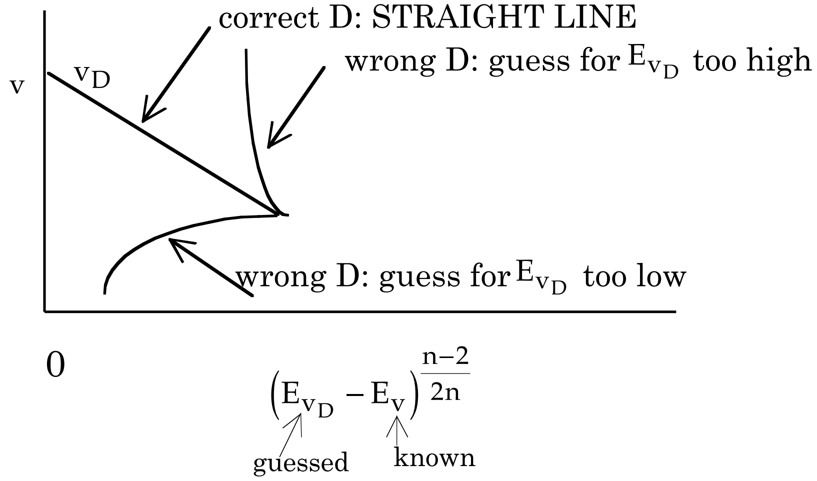
x^{-1} and x^{-2} potentials have ∞ number of bound levels. x^{-3}, x^{-5}, x^{-6} potentials have finite number, and the number of levels breaks off more abruptly as n increases.



i.e., # of bound levels

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

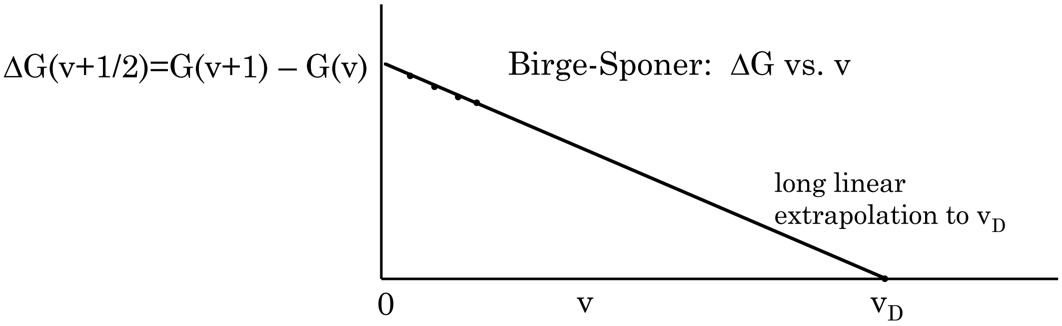
This means (equation at bottom of 8-9) that if we plot (given that we can predict n with certainty)



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

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

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

$v_D = \frac{\omega_e}{2\omega_e x_e} - 1$ 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

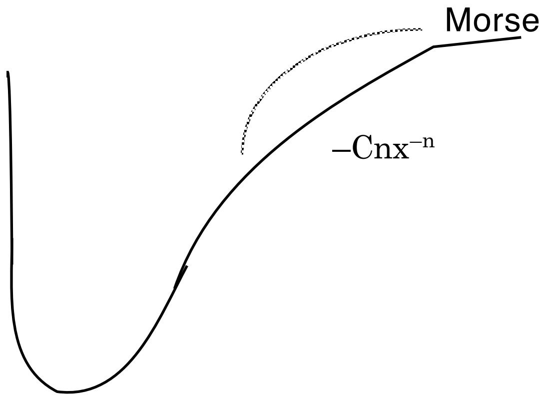
Which is longer range? Morse or $C_n x^{-n}$? Take ratio of binding energy at large x.

$$\lim_{x\to\infty}\frac{-C_n x^{-n}}{D\left[1-e^{-Ax}\right]^2-D}=\lim_{x\to\infty}\frac{-C_n x^{-n}}{De^{-2Ax}-2De^{-Ax}}$$

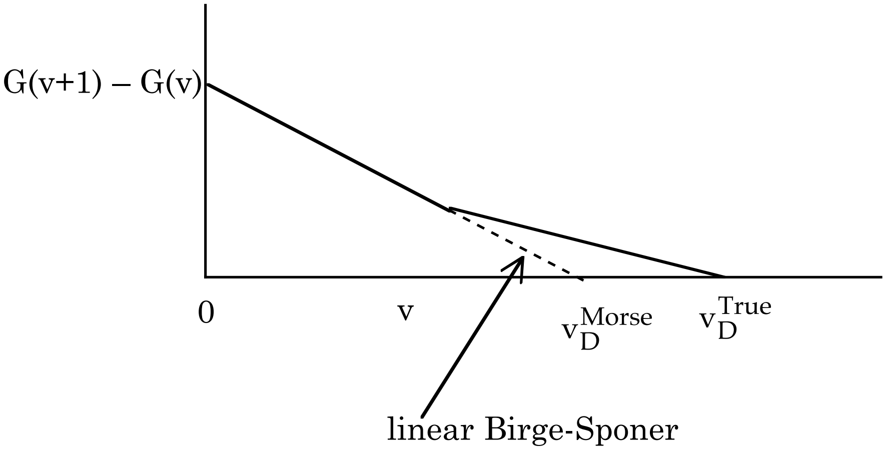
$$=\lim_{x\to\infty}\frac{-C_n x^{-n}e^{2Ax}}{D-\boxed{2De^{Ax}}}\longleftarrow\text{dominant term}$$

$$=\lim_{x\to\infty}\frac{C_n}{2D}x^{-n}e^{Ax}\to\infty$$

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.