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

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

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

But where do we get $V(x)$? Certainly not from femtochemistry! From FREQUENCY DOMAIN SPECTROSCOPY $E_{v,J} \rightarrow V(x)$

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

$$A(E, J) =$$

Long Range Theory: Ultra Cold Collisions: Atom in Molecule
Someday you will discover that the energy levels of a diatomic molecule are given by

\[ E_{\text{evJ}}/\hbar c = T_e + G(v) + F_\text{rotation}(J) \text{ cm}^{-1} \]

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

\[ + \left[ B_e - \alpha_e (v + 1/2) + \ldots \right] J(J+1) - DJ^2 (J+1)^2 \]

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} \]

\[ x \equiv R - R_e \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

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.

\[ \int_{x_- (E_v)}^{x_+ (E_v)} p_{E_v} (x') dx' = (\hbar/2)(v + 1/2) \]

\( v = 0, 1, \ldots \# \text{ of nodes} \)

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!

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

\[ \text{area at } E \]

\[ x_-(E) \quad x_+(E) \]
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

2. independently, \( \frac{\partial A}{\partial E} \) and \( \frac{\partial A}{\partial J} \) determine

\[
\begin{bmatrix}
[x_+(E,J) - x_-(E,J)] & \frac{1}{x_+(E,J)} - \frac{1}{x_-(E,J)}
\end{bmatrix}
\]

2 eqs. in 2 unknowns give turning points

Do #2 first because it is so easy

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

\[
= \int_{x_-}(E,J) 1 dx' + 0 + 0
\]

Contributions from \( \frac{dx_+(E,J)}{dx} \) are zero because integrand is 0 at turning points

\[
\frac{\partial A}{\partial E} = x_+(E,J) - x_-(E,J) \]

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

\[
= -\frac{\hbar^2}{2\mu} \int_{x_-}(E,J) \frac{2J+1}{x'^2} dx' + 0 + 0
\]

Integrand = 0 at \( x_\pm \)

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

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)

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

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

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 $J = 0$.

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

lower limit independent of $E$

integrand $= 0$ at upper limit

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

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

$$\begin{bmatrix}
G(v) = Y_{00} + \omega_{e}(v + 1/2) \\
0 = G(v_{\text{min}}) = Y_{00} + \omega_{e}(v_{\text{min}} + 1/2) \\
-\frac{Y_{00}}{\omega_{e}} = v_{\text{min}} + 1/2 \\
v_{\text{min}} = -\frac{Y_{00}}{\omega_{e}} - \frac{1}{2}
\end{bmatrix}$$

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

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

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

evaluate this integral numerically at any $E$.

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

updated 9/18/02 8:57 AM
\[
\frac{\partial A}{\partial J} \bigg|_{J=0} = \left( \frac{2\hbar^2}{\mu} \right) \int_{v(E)}^{v(E)} \left[ E - G(v) \right]^{-1/2} \frac{\partial E}{\partial J} \, dv + 0 + 0
\]

\[
E = B_J (J + 1)
\]

\[
\frac{\partial E}{\partial J} = B_v (2J + 1), \quad \frac{\partial E}{\partial J} \bigg|_{J=0} = B_v
\]

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

(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

\[
A(E, J) = 2 \left( \frac{2\hbar^2}{\mu} \right) \int_{v(E)}^{v(E)} \left[ E - V_J(x) \right]^{1/2} \, dx
\]

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} \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)} 2 \pi \left( \frac{E}{\nu_{vJ}(x)} \right) \left( \frac{E'_{\nu J} - V_J(x')}{E - E'_{\nu J}} \right)^{1/2} dE'_{\nu J} \right) dx' \quad \text{reverse order of integration and recognize WKB QC in disguise}

\frac{2}{\pi} \int_{x_-(E, J)}^{x_+(E, J)} \left( \frac{E'_{\nu J} - V_J(x')}{E - E'_{\nu J}} \right)^{1/2} dE'_{\nu J} \right) dx' \quad \text{numerator of } dx' \text{ integral is QC — insert QC and then integrate by parts.}

\text{denominator is independent of } x', \text{ so insert QC}

\int_{x_-}^{x_+} [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_{\text{min}}}^{E} \left[ \frac{v(E', J) + 1/2}{(E - E'_{\nu J})^{1/2}} \right] dE'_{\nu J} \quad **

** integrate by parts

\begin{align*}
f' &= (E - E'_{\nu J})^{-1/2} \\
f &= -2(E - E'_{\nu J})^{1/2} \quad \text{(not a typo because variable is } E'_{\nu J} \text{ not } E) \\
g &= [v(E'_{\nu J}, J) + 1/2] \\
g' &= \frac{dv}{dE'}, \quad \text{which is known from } E_{\nu J}
\end{align*}

A(E, J) = \left. \frac{fg}{E'_{\nu J}} \right|_{E'_{\nu J} = E_{\text{min}}} + \left( \frac{2h^2}{\mu} \right)^{1/2} \int_{E_{\text{min}}}^{E} 2(E - E')^{1/2} \frac{dv}{dE'} dE' \quad \text{(caution: } f \text{ and } g \text{ here are not Klein’s action integrals)}
** change variables from \(dE'\) to \(dv'\)

\[
dv = \frac{dv}{dE'} \cdot dE'
\]

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

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

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 \(x_\pm(E,0) = \left[ \frac{f(E)}{g(E)} + f(E)^2 \right]^{1/2} \pm f(E)\)

from quadratic formula

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

\[
V(x) \quad \text{connect the dots!}
\]

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 \(E - V(Q)\)
does not determine the multicomponent vector \(\mathbf{P}\)
Long-Range Molecules

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

\[ x_+(v_D) = \infty \]

\[ x_-(v) \]

\[ D \]

\[ \epsilon_v \equiv E_{v_D} - E_v \]

\[ v_D \] is noninteger \( v \)

of “level” at “top” of potential

\( \epsilon_v \) is binding energy of \( v \)-th level

at \( J = 0 \)

\[ V_0(x) = U(x) = -C_n x^{-n} \]

at long range (large \( x \))

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

\[ U(x_e) = -D_e \]

\[ x_+(v) = (-C_n / E_v)^{1/n} \]

\[ x_+(v_D) = \infty \]

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

How many levels are there in potential?

\[ \frac{\hbar}{2} \left( v_D + \frac{1}{2} \right) = \int_{x_-(v_D)}^{x_+(v_D) = \infty} p_D(x') dx'. \]

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

\[ v_D - v = a_n \epsilon_v^{2/n} \]

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
- 3 dipole - dipole (also transition dipoles)
- 5 dipole - induced dipole
- 5 quadrupole - quadrupole
- 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 $\Delta H_f^\circ$). Now Bose condensates. Molecule trapping.

$x^{-1}$ and $x^{-2}$ potentials have $\infty$ 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.

Action integral affected more by wider classical $\Delta x$ region than by deeper $\Delta E$ 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)

\[
\begin{align*}
\text{correct } D : \text{STRAIGHT LINE} \\
\text{wrong } D : \text{guess for } E_{vD} \text{ too high} \\
\text{wrong } D : \text{guess for } E_{vD} \text{ too low}
\end{align*}
\]

\[
\left( E_{vD} - E_v \right)^{\frac{n-2}{2n}}
\]

\[\frac{\text{guessed}}{\text{known}}\]

\[
\begin{array}{c|c}
 n & \frac{n-2}{2n} \\
\hline
 3 & \frac{1}{6} \\
 5 & \frac{3}{10} \\
 6 & \frac{1}{3} \\
 7 & \frac{5}{14}
\end{array}
\]

it is possible to determine \( D \) and \( v_D \) very accurately

\[
\begin{align*}
\Delta G(v+1/2) &= G(v+1) - G(v) \\
\text{for } \text{Morse} \\
G(v) &= \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 \\
\Delta G(v+1/2) &= G(v+1) - G(v) = \omega_e - \omega_e x_e (2v + 2) \text{ decreasing to 0 as } v \text{ increases}
\end{align*}
\]

Morse Potential

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

\[
v_D = \frac{\omega_e}{2\omega_e x_e} - 1 \quad v_D \text{ is noninteger # of bound vibrational levels}
\]

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

\[
= \left( v_D + 1 \right) \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} \approx \left( v_D + 1 \right) \frac{\omega_e}{2}
\]

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 $x$.

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

\[
= \lim_{x \to \infty} \frac{-C_n x^{-n} e^{2A x}}{D - 2D e^{A x}} \quad \text{dominant term}
\]

\[
= \lim_{x \to \infty} \frac{C_n x^{-n} e^{A x}}{2D} \to \infty
\]

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 $E_{vD} - E_v$ gives more accurate dissociation energy.