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

**WKB Quantization Condition**

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

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

$E_n$ without $\psi_n$!

But where do we get $V(x)$?
Certainly not from femtochemistry!
From FREQUENCY DOMAIN SPECTROSCOPY

$E_{v,J} \rightarrow V(x)$? Energy levels as function of quantum numbers $\rightarrow$ potential energy as function of coordinate, $V(x)$.

**RKR method**

Next time: Numerical Integration of 1-D Schr. Eq. — See handouts.
Then we will begin working toward matrix picture

We will need background in Chapter 2 of CTDL, pages 94-121 soon, pages 121-144 by next week

Postulates and Theorems will not be covered except as needed for solving problems

Today: $E_{v,J}$ $\rightarrow$ spectroscopic notation: cm$^{-1}$ units, $T$ electronic, $G$ vibrational, $F$ rotational

Area: $A(E,J) =$

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

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

WKB Quantum Condition applied to $\frac{\partial A}{\partial E}, \frac{\partial A}{\partial J}$ 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
\[
\frac{E_{evJ}}{\hbar c} = T_e + G(v) + F_v(J) \quad \text{cm}^{-1} \\
= \nu_e + \left[ Y_{\nu_0} + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \ldots \right] \\
+ \left[ B_e - \alpha_e (v + 1/2) + \ldots \right] J(J+1) - DJ^2(J+1)^2
\]

RKR requires only \(G(v)\) and \(B(v)\) spectroscopic data to get \(V_J(x)\)

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

\[\mu = \frac{m_1m_2}{m_1+m_2}\]

We are going to derive \(V_0(x)\) directly from \(G(v), B(v)\) data. This is the only direct spectrum to potential energy function inversion method! WKB quantization is the basis for this. It is easy to go from \(V_0(x)\) to \(G(v), B(v)\), but RKR is special. Many methods work in the opposite direction to get \(G(v)\) and \(B(v)\) from \(V_0(x)\). We start with the WKB quantization condition:

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

In this equation, what we know \((E_v)\) and what we want \((V(x)\) and \(x\) at turning points) are hopelessly intermixed. There is a trick to disentangle them!

\[
A(E,J) \equiv \int_{x_-(E,J)}^{x_+(E,J)} [E - V_J(x')]dx' \quad \text{area at } E
\]
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 \( E_{v,J} \) information

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

\[
\left[ x_+(E,J) - x_-(E,J) \right] \quad \text{and} \quad \left[ \frac{1}{x_+(E,J)} - \frac{1}{x_-(E,J)} \right]
\]

Do #2 first because it is so easy

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

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

Contributions from \( \frac{\partial A}{\partial E} \) are zero because integrand is 0 at both turning points

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

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

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

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 \( E_{vJ} \) 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)

$$A(E,J) = \int_{x_{(E,J)}}^{x_{(E,J)}} \left[ E - V_f(x') \right] dx'$$  
(change variables from $x$ to $v$)

$$A(E,J) = 2\pi \int_{v_{(E,J)}}^{v_{(E,J)}} \left[ E - E'_{vJ} \right]^{1/2} dv$$  
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 $J = 0$.

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

lower limit dependent of E

integrand = 0 at upper limit

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

defined so that $G(v_{\text{min}}) = 0$ this occurs at $v_{\text{min}} \neq -1/2$

$$G(v) = Y_{00} + \omega_e \left(v + 1/2\right)$$

$$0 = G(v_{\text{min}}) = Y_{00} + \omega_e \left(v_{\text{min}} + 1/2\right)$$

$$-\frac{Y_{00}}{\omega_e} = v_{\text{min}} + 1/2$$

$$v_{\text{min}} = -\frac{Y_{00}}{\omega_e} - \frac{1}{2}$$

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

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

evaluate this integral numerically at any $E$.

[Singularity at upper limit of integration fixed by change of variable; Zeleznik *JCP* 42, 2836 (1965).]
Nonlecture derivation of this useful form of $A(E,J)$:

$$A(E,J) = 2\pi \int_{v_{vJ}^{\min}}^{v_{vJ}^{(E,J)}} \left[ E - E_v^{J'} \right]^{-1/2} dv$$

Begin here:

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

an integral identity:

$$b - a = \frac{2}{\pi} \int_{a}^{b} \frac{(x - a)}{(b - x)}^{1/2} dx$$

let

$$b = E$$

$$a = V_{J}(x)$$

$$x = E_v^{J'}$$

so that

$$\left( \frac{x - a}{b - x} \right) = \frac{E_v^{J} - V_{J}(x)}{E_{vJ} - E_v^{J}}$$

Thus,

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

Now insert the integral identity

(again, a nonfatal singularity at upper limit of integration)

$f(E)$ and $g(E)$ are “Klein action integrals” which are jointly determined by empirical $G(v)$ and $B(v)$ functions.
5.73 Lecture #8  
Rydberg Klein Rees

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

put in values of \(a, b,\) and \(x\)

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

Reverse order of integration and recognize the WKB QC in disguise:

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

Numerator of \(dx'\) integral is QC — insert QC and then integrate by parts. Denominator is independent of \(x'\), so insert QC

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

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

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

** integrate by parts

\[
f' = (E - E_{vJ})^{-1/2} 
\]

\[
f = -2(E - E_{vJ})^{1/2} 
\]

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

\[
g' = \frac{dv}{dE'}, \quad \text{which is known from } E_{vJ} \quad (\text{not a type because the variable is } E_{vJ}, \text{ not } E) 
\]

\[
A(E, J) = \left. f g \right|_{E' = E_{min}}^{E' = E} + \left( \frac{2h^2}{\mu} \right)^{1/2} \int_{E_{min}}^E 2(E - E')^{1/2} \frac{dv}{dE'} dE' 
\]

\[
= 0 \text{ at both limits} 
\]

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

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*** Change variables from $dE'$ to $dv'$

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

limits of integration become $\int_{v(E_{\text{min}}, J)}^{v(E, J)} dv' = \int_{v(E_{\text{min}}, J)}^{v(E, J)} dE'$

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

we have independent evaluations of both $f(E)$ and $g(E)$ from $G(v)$ and $B(v)$ data

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

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

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!

can use very fine grid of $E$'s.

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

http://leroy.uwaterloo.ca/programs.html

Download program, instructions, and sample data.

RKR does not work for polyatomic molecules because $E - V(Q)$ does not determine the multicomponent vector $\vec{P}$ (one component for each normal mode).
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 region of the outer turning point. 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 should be insensitive to details near both $x_o$ and the inner turning point).

$$A(E,J) = \int_{x_a}^{x_b} [b - a] dx'$$ (See page 8-5)

What do we know about covalent bonding?

ATOMIC ORBITAL OVERLAP IS REQUIRED!

NEGLECTIBLE OVERLAP at large $x$, $V(x)$ at large $x$ is determined by properties of isolated atoms: dipole moment, polarizability — return to this later when we do perturbation theory.

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

It is always possible to predict what is 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

\[ \begin{align*}
\varepsilon_v &\equiv E_{vD} - E_v \\
x_+(vD) &= \infty \\
v_D &\text{ is non-integer value of } v \\
\text{of the “Level” at the “top” of the potential}
\end{align*} \]

\[ \begin{align*}
\varepsilon_v &\equiv E_{vD} - E_v \\
x_+(vD) &= \infty \\
\text{of v-th level, } \varepsilon_v &\equiv E_{vD} - E_v
\end{align*} \]

\[ \begin{align*}
\text{at } J = 0 \\
V_0(x) &= U(x) = -C_n x^{-n} \\
U(\infty) &= 0 \equiv E_{vD} \\
U(x_e) &= -D_e \\
x_+(v) &= \left(-\frac{C_n}{E_v}\right)^{1/n} \\
E_v &= V(x_+(v)) = -C_n x_+^{-n}
\end{align*} \]

at long range (large x)

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

How many bound levels are there in the potential? WKB Quantization Condition:

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

Now we do not know \( v_D, C_n \), or \( D_e \), but we do know \( n \) and know that \( E_v \) will be primarily determined by the 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

\[ (v_D - v) \# \text{ of levels below highest bound level} \]

and

\[ (E_{vD} - E_v) \text{ binding energy}. \]

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

\[ v_D - v = a_n \varepsilon_v^{-2n}. \]

This equation tells us how to plot \( E_v \) vs. \( v \) to extrapolate to \( v_D \) and then to obtain an accurate value of \( D_e \) from a linear plot near dissociation.
$V(x) = C_n x^{-n}$ for 2 Atoms [CTDL, page 283]

1. Both atoms are charged
2. One Atom is charged, the other atom has permanent electric dipole
3. 2 identical uncharged atoms with transition dipole moments e.g. Na(\text{P}) + Na(\text{S})
4. charge-induced dipole and dipole-quadrupole
5. quadrupole-quadrupole
6. induced dipole-induced dipole (London dispersion)

The interaction with smallest $n$ is dominant at long-range

Not only is the limiting value of $n$ 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 are now used to determine $V(x)$ to very large $x$. This has now become the 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 determination of $\Delta H_f^\circ$). Now Bose condensates. Molecule trapping.

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

\[
\text{i.e., # of bound levels}
\]

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 page 8-9) that if we plot (given that we can predict \( n \) with certainty) as shown below.

\[
\begin{align*}
\Delta G(v+1/2) &= G(v+1) - G(v) \\
&= \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2
\end{align*}
\]

\[
G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2
\]

\[
\Delta G(v+1/2) = G(v+1) - G(v) = \omega_e - \omega_e x_e (2v + 2) \text{ decreasing to 0 as } v \text{ increases}
\]

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

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

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

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

But Morse potential inevitably has incorrect long-range form!

\[\text{updated 8/13/20 1:05 PM}\]
Which potential curve is longer range? Morse or $C_n x^{-n}$? Take ratio of binding energy at large $x$.

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

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

$$= \lim_{x \to \infty} \frac{C_n x^{-n} e^{4Ax}}{2D_e} \to \infty$$

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

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

Dissociation energy is usually underestimated by linear Birge-Sponer extrapolation. Long-range plot of correct (a priori known) power of $E_{v_0} - E_v$ gives more accurate dissociation energy.