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

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

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

\( E_n \) without \( \psi_n \)!

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

**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.

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Today: \( E_{v,J} \rightarrow \) spectroscopic notation
\( A(E,J) = \)

\[
E
\]

\[
V(x)
\]

\[
\text{Equilibrium } \frac{dV}{dx} = 0 \rightarrow x_e
\]

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

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

\[ E_{evJ} / hc = T_e + \frac{G(v)}{vibration} + \frac{F_v(J)}{rotation} \text{ cm}^{-1} \]

\[ = \nu_e + \left[ Y_{00} + \frac{\omega_e(v + 1/2) - \omega_xe(v + 1/2)^2 + \ldots}{C(v)} \right] \]

\[ + \left[ \frac{B_v - \alpha_e(v + 1/2) + \ldots}{B(v)} \right] J(J+1) - DJ^2(J+1)^2 \]

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

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

\( x \equiv R - R_e \)

\( \mu = \frac{m_1 m_2}{m_1 + m_2} \)

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.

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

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

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

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

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

Do #2 first because it is so easy

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

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

contributions from $\frac{\partial A(x,E)}{\partial E}$ are zero because integrand is 0 at turning points

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

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

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

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 $E_{vd}$ data, we have $V_d(x)$!
some clever manipulations to put \( A(E,J) \) into convenient form
(see nonlecture notes on pages 8-5, 6, 7)

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

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

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 \( J = 0 \).

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

integrand = 0

lower limit independent of \( E \)

at upper limit

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

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

evaluate this integral numerically at any \( E \).

[Singularity at upper limit fixed by change of variable: Zeleznik JCP 42, 2836 (1965).]
\[ \frac{\partial A}{\partial J} \bigg|_{J=0} = \left( \frac{2\hbar^2}{\mu} \right)^{1/2} \int_{-1/2-Y_{00}/\omega_c}^{v(E)} \left[ E - G(v) \right]^{-1/2} \frac{\partial E}{\partial J} \, dv + 0 + 0 \]

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

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

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

(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

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

Begin here:

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

Integral identity

\[ b - a = \frac{2}{\pi} \int_{a}^{b} \frac{\left( x - a \right)^{1/2}}{b - x} \, dx \]

let \[ b = E \]

\[ a = V_J(x) \]

\[ x = E_{vJ} \]

so that

\[ \frac{x - a}{b - x} = \frac{E_{vJ} - V_J(x)}{E - E_{vJ}} \]

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

Now insert the integral identity

\[ \text{updated 9/18/02 8:57 AM} \]
A(E, J) = \int_{x_-(E, J)}^{x_+(E, J)} \left( \frac{2}{\pi} \right) \left( \frac{x - a}{b - x} \right)^{1/2} dx \right) dx' 

\text{reverse order of integration and recognize WKB QC in disguise}

\int_{x_-(E, J)}^{x_+(E, J)} \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}

\text{numerator of } dx' \text{ integral is QC — insert QC and then integrate by parts. denomenator is independent of } x', \text{ 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'_{vJ} \quad **

** integrate by parts

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

f = -2\left( E - E_{vJ} \right)^{1/2} \quad \text{(not a typo because variable is } E_{vJ} \text{ not } E)\n
g = \left[ v(E_{vJ}', J) + 1/2 \right]

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

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' \quad \text{(caution: } f \text{ and } g \text{ here are not Klein's action integrals)}
** change variables from dE' to dv'

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

limits of integration become

\[ \int_{v(E_{\text{min}},J)}^{v(E,J)} [E - E'_{J}]^{1/2} \, dv \]

finished:

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

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!

\[ V(x) \]

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 \( \sim \) does not determine the multicomponent vector \( \mathbf{P} \)

updated 9/18/02 8:57 AM
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

\[ \varepsilon_v \equiv E_{vD} - E_v \]

\[ x_-(v) \]

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

\[ \varepsilon_v \] is binding energy of \( v \)-th level

at \( J = 0 \)

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

at long range (large \( x \))

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

\[ U(x_c) = -D_c \]

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

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

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

How many levels are there in potential?

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

Now we do not know \( vD, C_n, \) or \( D_c \), but we do know \( n \) and know that \( E_v \) will be primarily determined by long-range part of \( V(x) \) near \( vD \).

So, for any \( E_v \) we expect that it will be possible to derive a relationship between

\[ (vD - v) \]  

\# of levels below highest bound level

and

\[ (E_{vD} - E_v) \]  

binding energy

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

\[ \frac{n-2}{vD - v} = a_n \varepsilon_v^{2n} \]

Tells us how to plot \( E_v \) vs. \( v \) to extrapolate to \( vD \) and then to obtain accurate value of \( D_c \) 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)

\[
\frac{n-\frac{2}{n}}{\text{guessed}} = \frac{\left(E_{V_D} - E_V\right)^{\frac{n-2}{2n}}}{\text{known}}
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>( n-\frac{2}{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1/6</td>
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<tr>
<td>5</td>
<td>3/10</td>
</tr>
<tr>
<td>6</td>
<td>1/3</td>
</tr>
<tr>
<td>7</td>
<td>5/14</td>
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</tbody>
</table>

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

\[
\Delta G(v+1/2) = G(v+1) - G(v) = \omega_R(v+1/2) - \omega_x(v+1/2)^2
\]

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

for Morse

\[
G(v) = \omega_R(v + 1/2) - \omega_x(v + 1/2)^2
\]

Morse Potential

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

\[
v_D = \frac{\omega_R}{2\omega_x} - 1
\]

\( v_D \) is noninteger # of bound vibrational levels

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

\[
= (v_D + 1) \frac{\omega_R}{2} - \frac{\omega_x}{4} \approx (v_D + 1) \frac{\omega_R}{2}
\]

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 $x$.

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

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

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

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.