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# Lecture #21: Construction of Potential Curves by the Rydberg-Klein-Rees Method (RKR)

Go to <http://leroy.uwaterloo.ca/programs.html> for RKR1 [computes  $V(r)$  by RKR from  $G(v)$  and  $B(v)$ ] and LEVEL [numerical integration to get  $\chi_v(r)$  and compute many  $\langle v|\mathbf{O}p|v'\rangle$  integrals].

The RKR method is an accurate and convenient method of constructing a potential curve,  $V(r)$  from observed vibrational energy levels and rotational constants. To use the method one need only know or guess the variation of the vibrational energy and rotational constant with  $v$ , the vibrational quantum number. The RKR method generates inner and outer turning points ( $r_-$  and  $r_+$ , the two points on the potential curve corresponding to a specific energy) by numerical evaluation of two integrals involving the  $G(v)$  and  $B(v)$  functions. The potential curve is generated point-wise.

The validity of the RKR method rests on an approximate criterion for the existence of a vibrational eigenvalue at an energy  $E$ . This criterion is known as the Bohr-Sommerfeld quantization condition which can be derived by the WKB (Wentzel, Kramers, Brillouin) method in which the wave function is represented as a truncated asymptotic expansion. In what is called the “WKB approximation” or the “semi-classical approximation” the WKB wavefunction has the form

$$\psi = \left(\frac{p(r)}{\hbar}\right)^{-1/2} \exp\left(\pm \frac{i}{\hbar} \int_{r_{\pm}}^r p(r) dr\right) \quad (1)$$

where  $p(r)$ , the classical mechanical momentum at  $r$ , is by definition

$$p(r) = [2\mu(E - V(r))]^{1/2}. \quad (2)$$

This expression for  $\psi$  will be valid wherever the de Broglie wavelength  $\lambda$  is neither infinite nor rapidly varying with  $r$ .

$$\lambda(r) = \frac{\hbar}{p(r)} = \frac{\hbar}{[2\mu(E - V(r))]^{1/2}} \quad (3)$$

$|\lambda(r)| < \infty$  implies  $r$  is far from a turning point.  $\left|\frac{d\lambda}{dr}\right| \ll 1$  implies that  $\left|\frac{dV(r)}{dr}\right|$  is small, or that there are no kinks in the potential. We can summarize these requirements as

$$\left|\frac{\lambda \frac{dV}{dr}}{2(E - V)}\right| \ll 1.$$

The quantization condition that we need for the RKR method is

$$2 \int_{r_-}^{r_+} \frac{1}{\hbar} [2\mu(E - V(r))]^{1/2} dr = (2\nu + 1)\pi \quad (4)$$

or

$$\int_{r_-}^{r_+} p(r) dr = (h/2)(\nu + 1/2) \quad (\text{action integral}).$$

This condition arises from the requirement that the phase of  $\psi$  constructed inward from the left (inner) turning point must match up with the phase of  $\psi$  constructed inward from the right (outer) turning point.

$$\psi_{\text{left}}(r) \sim \cos \left[ \int_{r_-}^r \frac{p(r)}{\hbar} dr - \frac{\pi}{4} \right] \quad (5a)$$

$$\psi_{\text{right}}(r) \sim \cos \left[ - \int_r^{r_+} \frac{p(r)}{\hbar} dr + \frac{\pi}{4} \right] \quad (5b)$$

The difference in phase must be  $n\pi$

$$n\pi = \int_{r_-}^r \frac{p(r)}{\hbar} dr + \int_r^{r_+} \frac{p(r)}{\hbar} dr - \frac{\pi}{2} \quad (6)$$

$$\left( n + \frac{1}{2} \right) \pi = \int_{r_-}^{r_+} \frac{p(r)}{\hbar} dr. \quad (7)$$

The  $\pm \frac{\pi}{4}$  in equations (5) came from a method for connecting the WKB wave function inside the potential well to the WKB wave function outside by approximating the potential function at the turning point as linear in  $r$  and using the exact solution of the Schrödinger equation for a linear potential. This procedure is necessary because the WKB approximation is invalid at turning points. The connection procedure is valid if

$$\left| \frac{d^n V}{dr^n} \right| \ll 1 \text{ for } n > 1.$$

Note that this requirement is met exactly for a harmonic oscillator potential function.

The RKR method is based on a clever trick. The trick involves definition of a special function  $A(E, J)$  whose partial derivatives,  $\frac{\partial}{\partial E}$  and  $\frac{\partial}{\partial J}$ , are simple functions of the two turning points,  $r_+$  and  $r_-$ , and such that these derivatives may be expressed as integrals involving only the  $G(\nu)$ ,  $B(\nu)$  functions and the vibrational quantum number as the integration variable.  $G(\nu)$  is the vibrational energy expressed as some function of  $\nu$ .  $B(\nu)$  is the rotational constant expressed as a function of  $\nu$ . Since  $E = E(\nu, J)$  it is possible to unambiguously define  $\nu = \nu(E, J)$ . Although  $\nu, J$  are integers for observable energy levels,  $\nu$  and  $J$  will be regarded as continuously variable in any functional expression.

Let us define  $A(E, J)$

$$A(E, J) \equiv \int_{E_{\min}}^E \pi \left[ \nu(E', J) + \frac{1}{2} \right] [E - E']^{-1/2} dE' \quad (8)$$

where  $E_{\min}$  is the energy of the minimum of  $V(r)$ . The formula for integration by parts is

$$\int f' g = f g - \int f g' \quad (9)$$

Let

$$f' = (E - E')^{-1/2} \quad \text{thus} \quad f = -2(E - E')^{1/2} \quad (\text{derivative is with respect to } E')$$

$$g = v(E', J) + \frac{1}{2}$$

The  $fg$  part vanishes because  $f = 0$  for  $E' = E$  and  $g = 0$  when  $v(E_{\min}, J) = -\frac{1}{2}$ . Thus

$$A(E, J) = + \int_{E_{\min}}^E 2\pi \frac{dv(E', J)}{dE'} (E - E')^{1/2} dE' \quad (10)$$

Now change variables

$$A(E, J) = 2\pi \int_{-1/2}^{v(E, J)} [E - E(v, J)]^{1/2} dv \quad (11)$$

Thus

$$\frac{\partial A(E, J)}{\partial E} = \pi \int_{-1/2}^{v(E, J)} [E - E(v, J)]^{-1/2} dv \quad (12)$$

for  $J = 0$

$$\frac{\partial A(E, 0)}{\partial E} = \pi \int_{-1/2}^{v(E, 0)} [E - G(v)]^{-1/2} dv \quad (13)$$

and

$$\frac{\partial A(E, J)}{\partial J} = \pi \int_{-1/2}^{v(E, J)} [E - E(v, J)]^{-1/2} \frac{\partial E}{\partial J} dv \quad (14)$$

but

$$\frac{\partial E}{\partial J} = \frac{\partial}{\partial J} \{B(v)J(J+1) - D(v)J^2(J+1)^2 + \dots\} \quad (15)$$

$$= (2J+1)B(v) - (4J^3 + 6J^2 + 2J)D(v) + \dots \quad (16)$$

For

$$J = 0$$

$$\frac{\partial E}{\partial J} = B(v) \quad \text{exactly!}$$

Thus

$$\frac{\partial A(E, 0)}{\partial J} = \pi \int_{-1/2}^{v(E, 0)} B(v) [E - G(v)]^{-1/2} dv \quad (17)$$

Thus we have two very simple expressions for the derivatives of  $A(E, J)$  in terms of  $B(v)$  and  $G(v)$  in equations (13) and (17). Now we will re-express these derivatives in terms of the two turning points at energy  $E$ .

Return to the definition of  $A(E, J)$  in equation (8). The WKB eigenvalue condition of equation (4) may be re-written

$$\frac{1}{\hbar} \int_{r_-}^{r_+} [2\mu(E - V(r))]^{1/2} dr = \pi \left( \nu + \frac{1}{2} \right). \quad (18)$$

Rewrite  $V(r)$  as sum of two terms, a  $U(r)$  term which describes the potential function for  $J = 0$  (in the absence of rotation) and a term corresponding to the rotational energy  $\frac{\hbar^2 J(J+1)}{2\mu r^2}$ .

$$\frac{1}{\hbar} \int_{r_-}^{r_+} \left[ 2\mu(E - U(r)) - \frac{\hbar^2 J(J+1)}{r^2} \right]^{1/2} dr = \pi \left( \nu + \frac{1}{2} \right). \quad (19)$$

There is nothing fishy about this step. The square root is  $p(x)$  which by definition is  $(2\mu T)^{1/2}$  and  $T = E_{\text{TOT}} - E_{\text{ROT}} - U(r)$  where  $T$  is the kinetic energy.

Now plug equation (19) into equation (8):

$$A(E, J) = \int_{E_{\text{MIN}}}^E \frac{1}{\hbar} \int_{r_-}^{r_+} \left[ 2\mu(E' - U(r)) - \frac{\hbar^2 J(J+1)}{r^2} \right]^{1/2} [E - E']^{-1/2} dE' dr \quad (20)$$

In spite of the unnerving fact that the integrand diverges at  $E = E'$ , the upper limit of integration, the integral converges and is given by the following integral identity:

$$\int_a^b \left( \frac{x-a}{b-x} \right)^{1/2} dx = \int_a^b \left( \frac{b-x}{x-a} \right)^{1/2} dx = \frac{1}{2} \pi (b-a) \quad (21)$$

where  $b = E$ ,  $a = E_{\text{min}} = U(R) + \frac{\hbar^2}{2\mu r^2} J(J+1)$ . Thus

$$A(E, J) = \left( \frac{2\mu}{\hbar^2} \right)^{1/2} \frac{1}{2} \pi \int_{r_-}^{r_+} \left[ E - U(r) - \frac{\hbar^2}{2\mu r^2} J(J+1) \right] dr \quad (22)$$

$$\frac{\partial A}{\partial E} = \left( \frac{2\mu}{\hbar^2} \right)^{1/2} \frac{1}{2} \pi \int_{r_-}^{r_+} dr = \frac{\pi}{2} \left( \frac{2\mu}{\hbar^2} \right)^{1/2} (r_+ - r_-) \quad (23)$$

$$\frac{\partial A}{\partial J} = \left( \frac{2\mu}{\hbar^2} \right)^{1/2} \left( \frac{1}{2} \pi \right) \left( \frac{\hbar^2}{2\mu} \right) (2J+1) \int_{r_-}^{r_+} -\frac{1}{r^2} dr \quad (24)$$

$$\frac{\partial A}{\partial J} = \frac{1}{2} \pi \left( \frac{\hbar^2}{2\mu} \right)^{1/2} (2J+1) \left( \frac{1}{r_+} - \frac{1}{r_-} \right)$$

Combining equations (23) and (13)

$$r_+ - r_- = 2 \left( \frac{\hbar^2}{2\mu} \right)^{1/2} \int_{-1/2}^{\nu(E,0)} [E - G(v)]^{-1/2} dv \quad (25)$$

and combining equations (24) and (17)

$$\boxed{\frac{1}{r_+} - \frac{1}{r_-} = 2 \left( \frac{2\mu}{\hbar^2} \right)^{1/2} \int_{-1/2}^{v(E,0)} B(v) [E - G(v)]^{-1/2} dv} \quad (26)$$

We have two equations in two unknowns. The integrals in equations (25) and (26) are the Klein action integrals  $f$  and  $g$ , or specifically

$$\begin{aligned} r_+ - r_- &= 2 f(E) \\ \frac{1}{r_+} - \frac{1}{r_-} &= -2 g(E) \end{aligned} \quad (27)$$

Using the quadratic formula you can show that

$$r_{\pm} = (f/g + f^2)^{1/2} \pm f \quad (28)$$

Note that neither integral of equations (25) and (26) is well behaved at its upper limit of integration, but if the numerical integration is done properly the integrals converge. See A. Mantz, *et al. J. Mol. Spectrosc.* **39**, 180 (1971), for an article that demonstrates how well a potential curve constructed by the RKR method reproduces the  $G(v)$  and  $B(v)$  functions used to generate the potential curve. Even though  $G(v)$  and  $B(v)$  were needed to generate the potential curve, such a comparison is valid because once a potential curve is specified, it is possible by numerical methods to obtain the exact eigenfunctions from solution of the full radial Schrödinger equation. The procedure is as follows:

1. Construct the RKR potential curve.
2. Numerically obtain eigenfunctions and eigenvalues.
3. Compare eigenvalues with  $G(v)$  and compare  $\frac{\hbar^2}{2\mu} \left\langle v \left| \frac{1}{r^2} \right| v \right\rangle$  with  $B(v)$ .
4. Other properties of the molecule may be calculated by taking the appropriate matrix elements of any function of  $r$ . Franck-Condon factors may also be obtained.

A concluding note on the validity of the RKR method:

1. The Mantz *et al.* paper shows that RKR gives astonishingly accurate properties calculated from RKR curves.
2. RKR is based on the validity of WKB approximations. WKB is invalid near turning points, particularly when the two turning points are less than a de Broglie wavelength apart. Thus WKB is suspect near the bottom of any potential. However WKB wave functions are exact for the harmonic oscillator. Since the bottom of most molecular potentials is nearly harmonic, RKR should be an excellent approximation. At high vibrational levels RKR should be "exact."

Three valuable references are:

1. W. H. Miller, *J. Chem. Phys.* **54**, 4174 (1971).
2. R. N. Zare, *J. Chem. Phys.* **40**, 1934 (1964).
3. O. Klein, *Z. Phys.* **76**, 226 (1932).
4. S. M. Kirschner and J. K. Watson, *J. Mol. Spectrosc.* **47**, 234 (1973).