Rydberg-Klein-Rees method for determining potential energy curves of diatomic molecules from band spectra


O. Klein, Z. Physik 76, 226 (1932).


Empirically, the vibrational-rotational energy levels for a given electronic state of a diatomic molecule may be represented as a polynomial in \((v + \frac{1}{2})\) and \(J(J+1)\),

\[
E = \sum_{n,m} Y_{nm} (v + \frac{1}{2})^n [J(J+1)]^m,
\]

where \(Y_{nm}\) is called the "Dunham coefficient".

The simplest procedure, still used quite often, retains just the first few terms and matches coefficients with the corresponding series for some soluble potential model, such as the Morse potential,

\[
V(r) = D_e [e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}]
\]

Thus, e.g., in Herzberg's "bible" one finds the parameters tabulated refer to the empirical series

\[
\frac{E}{\hbar c} = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + B_e J(J+1) + D_e J^2(J+1)^2 - \alpha J(J+1)(v + \frac{1}{2}) + \ldots
\]

\[+ \omega_e y_e (v + \frac{1}{2})^3\]
For the Morse potential, find
\[ \frac{E}{\hbar c} = a \left( \frac{D_e \hbar}{2 \pi c \mu} \right)^{1/2} (\nu + \frac{1}{2}) - \frac{\hbar a^2}{2 c \pi \mu} (\nu + \frac{1}{2})^2 \]

without any higher powers of \( \nu + \frac{1}{2} \).

Thus identify
\[ \omega_e = a \left( \frac{D_e \hbar}{2 \pi c \mu} \right)^{1/2} \]

and evaluate \( a = \left( \frac{2 \pi c \mu}{D_e \hbar} \right)^{1/2} \omega_e \).

So that, if \( r_e, D_e, \) and \( \omega_e \) are known, the Morse curve is determined.

The Morse potential has the right qualitative form but it is not accurate enough for many purposes. The long-range part near the top of the well may be badly in error, as may the dissociation energy, and the axis of the well may be canted at the wrong angle. Many other potential models containing more adjustable parameters have been proposed but all have serious drawbacks.

The RKR procedure makes no special assumptions about the form of the potential, but rather employs the experimentally known energy levels to calculate points on the potential curve corresponding to the classical turning points of the nuclear motion. This determines very accurately pairs of points on \( V(r) \) up to the highest vibrational energy level known experimentally.

The RKR method has a simple physical interpretation. The two conditions required to evaluate the classical turning points \( r_- \) and \( r_+ \) of the vibrational motion at a given energy \( U \) may be represented in terms of the area enclosed by a line of constant energy and the effective potential energy curve, \( V_{\text{eff}}(r) \), as follows:

\[ \text{Area} = A = \int_{r_-}^{r_+} (U - V_{\text{eff}}) \, dr = \mathcal{S} (U, \nu) \]

\[ V_{\text{eff}}(r) = V(r) + \frac{K}{r^2} \]

with \( K = \frac{\mu p_0^2}{2} \) and \( \frac{K}{r^2} \) the centrifugal energy.
Now
\[
\left( \frac{\partial A}{\partial U} \right)_K = \int_{r_-}^{r_+} dr = r_+ - r_-
\]
\[- \left( \frac{\partial A}{\partial K} \right)_U = \int_{r_-}^{r+} \frac{dr}{r^2} = \frac{1}{r_-} - \frac{1}{r_+}
\]

Since \( U \) and \( K \) are related to the vibrational and rotational energies, \( A \) need only be expressible in terms of the experimental energy levels to determine \( r_+(U,K) \) and \( r_-(U,K) \) and hence obtain \( V(r) \). We can transform \( A \) from an integral over \( r \) to one over energy via

\[
U - V_{\text{eff}} = \frac{2}{\pi} \int_{V_{\text{eff}}}^{U} \left( \frac{U - E}{E - V_{\text{eff}}} \right)^{1/2} \frac{1}{dE}
\]

This is an "Eulerian integral of the first kind"

so that

\[
A(U,K) = \frac{2}{\pi} \int_{r_-}^{r_+} \frac{dr}{V_{\text{eff}}} \left( \frac{U - E}{E - V_{\text{eff}}} \right)^{1/2}
\]

\[
= \frac{1}{\pi} \int_{U_0}^{U} \frac{1}{(U - E)^{1/2}} \int_0^{\frac{1}{2}} \frac{dI}{(E - V_{\text{eff}})^{1/2}}
\]

where \( U_0 \) is the energy at the minimum of \( V_{\text{eff}} \).

Now we recall that the classical action integral for the radial momentum is

\[
I(E,K) = \oint p d\tau = (2\mu)^{1/2} \oint (E - V_{\text{eff}})^{1/2} d\tau
\]

and the associated vibrational period is given by

\[
\tau(E,K) = \frac{dI}{dE} = \left( \frac{U}{2} \right)^{1/2} \oint \frac{dI}{(E - V_{\text{eff}})^{1/2}}
\]

Hence have

\[
A(U,K) = \frac{1}{\pi} \int_{U_0}^{U} \frac{1}{(U - E)^{1/2}} \int_0^{\frac{1}{2}} \frac{dI}{(E - V_{\text{eff}})^{1/2}}
\]

\[
A(U,K) = \left( \frac{2}{\mu^2} \right) \int_0^{I'} (U - E)^{1/2} dI
\]

Note: at \( E = U_0 \), \( E = V_{\text{eff}} \)

and \( I = 0 \). At \( E = U \), denote by \( I' \) the value of \( I \) for which \( E(I,K) = U \)
We use the Bohr-Sommerfeld quantization rules to identify $I$ with $(v + \frac{1}{2})$ and $K$ with $J(J+1)$. Then, with $E(I,K)$ determined from the data as a power series in $I$ and $K$, the integral $A(U,K)$ can be evaluated. Then the variation in $A$ as $U$ is changed gives $r_+ - r_-$ and its variation as $V_{\text{eff}}$ is changed (by varying $K$) gives

$$\frac{1}{r_-} - \frac{1}{r_+} : r_+ (U,K) = \left( \frac{f}{g} + \frac{f^2}{g^2} \right) \pm f$$

Recall differentiation of an integral:

$$I(x,a,b) = \int_a^b f(x,y) dx$$

$$\frac{\partial I}{\partial x} = \frac{\partial I}{\partial a} \frac{\partial a}{\partial x} + \frac{\partial I}{\partial b} \frac{\partial b}{\partial x}$$

$$= \int_a^b \frac{\partial^2 f}{\partial x^2} dy - \frac{\partial a}{\partial x} f(x,a) - \frac{\partial b}{\partial x} f(x,b)$$

From the semiclassical quantization rules,

$$I = \oint p \delta dr = (v + \frac{1}{2}) \hbar$$

Since

$$K = \frac{p_0^2}{2\mu} \text{ and } \oint p \delta d\theta = 2\pi p_0 = (J + \frac{1}{2}) \hbar$$

and

$$K = \frac{J(J+1) \hbar^2}{8\pi^2 \mu}$$

In practice, the experimental energy levels are represented by a series quadratic in $v + \frac{1}{2}$ and $J(J+1)$:

$$E(I,K) = E(v + \frac{1}{2}, J(J+1))$$

$$= \omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2}^2 - \alpha(v + \frac{1}{2})J(J+1) + BJ(J+1) + DJ^2(J+1)^2 + ..$$
with $\omega$, $\omega x$, $\alpha$, $B$, $D$, ... constants. Usually $E(I,K)$ cannot be represented over the whole experimental range by a single such expression but can be represented as a quadratic over different regions so that the entire range can be covered with a series of quadratics. Then one uses

$$A(U,K) = \left(\frac{2}{\hbar \mu \pi^2} \right)^{1/2} \sum_{i=1}^{n} \int_{I_{i-1}}^{I_i} \left( a_i - b_i I_i + c_i I_i^2 \right)^{1/2} dI$$

where

$$a_i = h[U - B_i J(J+1) - D_i J^2 (J+1)^2 + ...]$$
$$b_i = \omega_i - \alpha_i J(J+1)$$
$$c_i = (\omega x)_i / h$$
$$I_0 = 0 \text{ and } I_n = I'$$

The summation extends over the vibrational energy levels.

For $J = 0$ states, obtain

$$f = \left(\frac{h}{8\pi^2 \mu c} \right)^{1/2} \sum_{i=1}^{n} \frac{1}{\sqrt{\omega x}_i} \ln W_i$$

$$g = \left(\frac{2\pi \mu c}{h} \right)^{1/2} \sum_{i=1}^{n} \left\{ \frac{2\alpha_i}{(\omega x)_i} \left[ (U_n - U_{i-1})^{1/2} - (U_n - U_i)^{1/2} \right] + \frac{1}{\sqrt{(\omega x)_i} \left[ 2B_i - \frac{\alpha_i}{(\omega x)_i} \omega_i \right]} \ln W_i \right\}$$

$$W_i = \left| \frac{[\omega_i^2 - 4(\omega x)_i U_i]^{1/2} - 2(\omega x)_i^{1/2} (U_n - U_i)^{1/2}}{[\omega_i^2 - 4(\omega x)_i U_{i-1}]^{1/2} - 2(\omega x)_i^{1/2} (U_n - U_{i-1})^{1/2}} \right|$$

$$r_{\pm} = \left( \frac{f}{g} + f^2 \right)^{1/2} \pm f$$

$f$, $r_{\pm}$ in cm; $g$, $U$, $\omega$, $\omega x$, $\alpha$, $B$ in cm$^{-1}$; energy zero min of $V(\pi)$, i.e. $U_0 = 0$.

In general, $\omega$, $\omega x$, $\alpha$, $B$ all vary with $\nu$. We get fair accuracy ($\sim 1\%$) with $\alpha$, $B$ held constant with $\nu$.

High accuracy evidently due to: (1) near minimum WKB energy levels are exact. (2) near dissociation limit, motion more nearly classical and first-order WKB again accurate.