The RKR Inversion Method ©

by

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The potential energy function is one of the central constructs of modern chemistry. It is based, theoretically, upon the Born-Oppenhiemer Approximation and can in principle, be calculated ab initio from the Schrodenger equation, with relativistic corrections for molecules that contain heavy atoms. Despite tremendous advances in the methods of Quantum Chemistry, calculated potentials, particularly for excited states, are often not of 'chemical accuracy', which is typically defined as an error of less than ~ 1 kcal/mole everywhere one the potential

High resolution spectroscopy provides a method to obtain potential surfaces that are typically orders of magnitude more precise than can be calculated ab initio. This arises from the ability to almost routinely measure vibration-rotation energy level differences with fractional accuracy of a part per million or better. The 'difficulty' is that what the chemist typically wants is not the eigenenergies, but the shape of the potential energy surface. If one knows the surface, one can solve the Schrodenger equation for the motion of the nuclei (using either perturbative or variational methods typically) and calculate the energies. It is possible to adjust the parameters in the functional form for the potential to get the 'best fit' to a set of data. While these methods are powerful and widely used, they are limited by the need to use a functional form, which likely can never be made to agree exactly with the 'true' potential that would in principle be predicted from an ab initio calculation done without error. This is not just a hypothetical assertion, but is the reason why the observed vibration-rotation energy level difference usually cannot be reproduced to within experimental error.

For diatomic molecules, there is a very power method known as the RKR (Rydberg-Klein-Rees) inversion which goes directly from the experimentally observed vibration-rotation energy level spacings to a potential energy function. This remarkable procedure is based upon a semiclassical approximation for the motion of the nuclei, but this itself tied to the Born-Oppenhiemer approximation. Because the electrons are much lighter than the nuclei, their wavelengths are much larger, and it is the wavelength of the valence electrons which determines the length scale over which the potential energy function changes. Since the nuclei have wavelengths much smaller than the length over which the potential energy changes significantly, the semiclassical treatment is typically an excellent approximation.
The RKR method is implemented as follows:

1. From the observed spectra involving a given electronic state, determine the vibrational energy and rotational constant for as wide a range of vibrational quantum number as possible.

2. Fit the vibrational energies, known for integer values of the quantum number \( v \), to a continuous function \( G(v) \). For lower quantum numbers, a Dunham expansion as powers in \( (v+1/2) \) is almost universally used. For higher states, where the Dunham expansion may be having convergence difficulties, a cubic spline or other interpolation method can be used. For the highest state, near to dissociation limit, a form introduced by LeRoy and Bernstein can be used. Likewise, a continuous function, \( B(v) \), for the rotational constant as a function of quantum number \( v \) is also determined from the experimental data.

You may be suspecting that introducing this functional fit for \( G(v) \) and \( B(v) \) is no different in principle than introducing a fit directly to the potential. However, when the Born-Oppenheimer approximation is valid, we expect that the discrete values (i.e. integers) that these functions are known are close enough together that \( G(v) \) and \( B(v) \) should change smoothly between quantum levels. As long as we do an excellent job of fitting the observed data with physically reasonable (i.e. smooth) functions, then the final potential predicted by the RKR inversion will be very similar.

3. We define two new functions

\[
f(v) = C \int_{-1/2}^{v} \frac{1}{\sqrt{G(u) - G(v)}} \, du
\]

\[
g(v) = \frac{1}{C} \int_{-1/2}^{v} \frac{B(u)}{\sqrt{G(u) - G(v)}} \, du
\]

With constant \( C \) defined by:

\[
C = \frac{\hbar}{\sqrt{8 \cdot \pi^2 \cdot c \cdot \mu}}
\]

where \( \hbar \) is Plank's constant, \( c \) the speed of light in vacuum, and \( \mu \) the reduced mass for the diatomic molecule.

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4. In terms of these new functions, we can calculate the inner and outer turning points of the potential as a function of quantum number $v$:

$$r_{\text{inner}}(v) = \sqrt{f(v)^2 + \frac{f(v)}{g(v)}} - f(v)$$

$$r_{\text{outer}}(v) = \sqrt{f(v)^2 + \frac{f(v)}{g(v)}} + f(v)$$

The potential, $V(r)$ is now defined by the equations

$$V(r_{\text{inner}}(v)) = V(r_{\text{outer}}(v)) = G(v)$$

Thus by varying $v$ in small steps, we can calculate $V = G(v)$ and $r$ values that give each such energy, and thus have a continuous representation of the energy. Thus we are done!

Many individuals only report $r_{\text{inner}}(v)$, $r_{\text{outer}}(v)$ and $G(v)$ for integer values of $v$, making it look like each particular vibrational level 'determines' its own inner and outer turning points. However, it can be seen from the definitions given above that $f(v)$ & $g(v)$, and thus $r_{\text{inner}}(v)$ and $r_{\text{outer}}(v)$ depend upon $G(u)$ and $B(u)$ for all values $-1/2 < u < v$, not just the integer values. The entire procedure is based upon a semiclassical treatment where $h(v+1/2)$ is just the energy dependent classical action per cycle of the classical oscillation in the well. That is why there is the 'funny' lower limit of $-1/2$ on the integrals; this just corresponds to the classical action being zero, which is the particle at rest at the bottom of the well. The point is that the potential calculated for noninteger points $v$ is not significantly less accurate than for integer values, and there is no need to only report those values.

The one important caveat to the above is that our functions $G(v)$ and $B(v)$ become unreliable if $v$ is significantly outside the range of observed quantum numbers of the states used to determine these functions, i.e. if we are making an extrapolation instead of an interpolation.
The only 'trick' to this procedure is in the evaluation of the integrals used to define the functions f(v) and g(v). As defined, f(v) and g(v) have singularities at the upper limit of their integrals. These properties cause 'general' numerical integration methods to have difficulty or even lack of convergence with these integrals. One needs a method that properly accounts for the singular behavior of the integrands. A particularly nice method was introduced by Joel Tellinghuisen, J. Molecular Spectroscopy 44, 194-196 (1972), who showed that it is possible to get six figure accuracy by using a four point numerical integration! One introduces the constants:

\[
\begin{align*}
  x_0 &:= -0.84431321698 & H_0 &:= 0.28631753784 \\
  x_1 &:= -0.26935495247 & H_1 &:= 0.62898854988 \\
  x_2 &:= 0.44763137226 & H_2 &:= 0.88729638641 \\
  x_3 &:= 0.93270346386 & H_3 &:= 1.02582465061
\end{align*}
\]

Mehler's quadrature is used to evaluate the integrals by the following expressions:

\[
\begin{align*}
  f(v) &:= C \cdot \frac{(v + 0.5)}{2} \sum_{i=0}^{3} H_i \sqrt{1 - x_i} \cdot \frac{1}{\sqrt{G(v) - G\left(\frac{v - 0.5}{2} \cdot x_i\right)}} \\
  g(v) &:= \frac{1}{C} \cdot \frac{(v + 0.5)}{2} \sum_{i=0}^{3} H_i \sqrt{1 - x_i} \cdot \frac{B\left(\frac{v - 0.5}{2} \cdot x_i\right)}{\sqrt{G(v) - G\left(\frac{v - 0.5}{2} \cdot x_i\right)}}
\end{align*}
\]

These equations are 'toggled off' because we have yet to define the functions G(v), B(v) and the constant C.
Let us now demonstrate this using as an example, $^{12}$C$^{16}$O. From a fit of up to $v=37$ ($\sim 63000$ cm$^{-1}$), the following constants have been determined (in units of cm$^{-1}$):

$$G(v) := 2169.8136 \left( v + \frac{1}{2} \right) - 13.2883 \left( v + \frac{1}{2} \right)^2 + 0.010512 \left( v + \frac{1}{2} \right)^3 \ldots$$

$$+ 5.74165 \cdot 10^{-5} \left( v + \frac{1}{2} \right)^4 + 9.833657 \cdot 10^{-7} \left( v + \frac{1}{2} \right)^5 - 3.1660555 \cdot 10^{-8} \left( v + \frac{1}{2} \right)^6$$

$$B(v) := 1.93128026 - 0.01750428 \left( v + \frac{1}{2} \right) + 5.48424213 \cdot 10^{-7} \left( v + \frac{1}{2} \right)^2 + 2.5318 \cdot 10^{-8} \left( v + \frac{1}{2} \right)^3$$

Let us define some constants:

- $c = 2.99792458 \cdot 10^8 \text{ m} \cdot \text{sec}^{-1}$: speed of light in vacuum
- $u = 1.6605402 \cdot 10^{-27} \text{ kg}$: Unified atomic mass constant a.k.a. amu or Dalton
- $h = 6.6260755 \cdot 10^{-34} \text{ joule} \cdot \text{sec}$: Planck's Constant
- $A_s = 10^{-10} \text{ m}$
- $\mu := \frac{16 \cdot 12}{16 + 12} u$  
- $C := \sqrt{\frac{h \cdot \text{cm}}{8 \cdot \pi^2 \cdot \text{c} \cdot \mu}}$  
- $C = 1.56793 A_s$

$$f(v) := C \frac{(v + 0.5)}{2} \sum_{i=0}^{3} H_i \sqrt{1 - x_i} \frac{1}{\sqrt{G(v) - G(\frac{v - 0.5}{2} + \frac{v + 0.5}{2} \cdot x_i)}}$$

$$g(v) := \frac{1}{C} \frac{(v + 0.5)}{2} \sum_{i=0}^{3} H_i \sqrt{1 - x_i} \frac{B(\frac{v - 0.5}{2} + \frac{v + 0.5}{2} \cdot x_i)}{\sqrt{G(v) - G(\frac{v - 0.5}{2} + \frac{v + 0.5}{2} \cdot x_i)}}$$

$$r_{\text{inner}}(v) := \left( \sqrt{f(v)^2 + \frac{f(v)}{g(v)} - f(v)} \right)$$

$$r_{\text{outer}}(v) := \left( \sqrt{f(v)^2 + \frac{f(v)}{g(v)} + f(v)} \right)$$

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Let us create arrays with the $r$ and $V$ values for steps of $v = 0.1$ from -0.5 to 35. We will first 'march down' the inner wall and then 'march up' the outer wall. Note: the above expressions are singular for $v = -1/2$, so we will calculate that point directly, noting this is the bottom of the well, so $r = r_0$, which can be calculated from $B_0 = B(-1/2)$.

First, the inner wall:

\[ i := 0..354 \]
\[ v_i := 0.1 \cdot (350 - i) \quad r_i := r_{\text{inner}}(v_i) \quad V_i := G(v_i) \]

The point $r_0$:

\[ v_{355} := -0.5 \]
\[ r_{355} := \frac{C}{\sqrt{B(-0.5)}} \quad V_{355} := G(-0.5) \]

Now, the outer wall:

\[ i := 356..710 \]
\[ v_i := 0.1 \cdot (i - 360) \quad r_i := r_{\text{outer}}(v_i) \quad V_i := G(v_i) \]

\[ i := 0..700 \quad \text{Plot of RKR curve for CO ground state} \]
Problem

1. Verify that the numerical integration expression 'works' by comparing the values of \( f(v) \) and \( g(v) \) for some fixed \( v \) using Mathcad's integrator with various values of the TOL function. You may run into convergence problems. This can be handled by splitting the integration interval into 3 parts, one near the singularity at the inner turning point, the center of the interval, and one near the outer turning point. The functions to be integrated near the singular end points diverge \( \sim \frac{A}{\sqrt{x}} \) where \( x \) is the distance from the turning point. This will have an integral \( 2A \sqrt{x} \). Thus the divergence near the singular end points can be integrated in such a manner.