2.4.5 "Approximate" method based on data

a) The RKR [Rydberg, Klein, Rees] method is based on the WKB approximation.

\[ U = U_{\text{pot}} + U_{\text{rad}} + U_{\text{int}} = E \]
\[ = U_{\text{pot}} + \frac{\hbar^2}{2mR^2} + \frac{p^2}{2m} \]
\[ V_{WKB}(R) \equiv U_{\text{pot}} + \frac{k}{R^2} \]

We have
\[ A = \int_{R_1}^{R_2} dR \left( U - U_{\text{pot}} - \frac{k}{R^2} \right) \]
\[ \text{Let assume } U \text{ a continuous variable} \]
\[ = 0 \quad \left( \frac{\partial A}{\partial u} \right)_{k=\text{const}} = \int_{R_1}^{R_2} dR = R_2 - R_1 \]
\[ + \left( \frac{\partial A}{\partial k} \right)_{u=\text{const}} = -\int_{R_1}^{R_2} \frac{dR}{R^2} = \frac{1}{R_2} - \frac{1}{R_1} \]

Writing
\[ f = \frac{1}{2} \left( \frac{\partial A}{\partial u} \right)_{k} = \frac{1}{2} \left( R_2 - R_1 \right) \]
\[ g = \frac{1}{2} \left( \frac{\partial A}{\partial k} \right)_{u} = \frac{1}{2} \left( \frac{1}{R_2} - \frac{1}{R_1} \right) \]
\[ \Rightarrow R_1 = \sqrt{\frac{f}{g} + f^2} - f \quad \text{and} \quad R_2 = \sqrt{\frac{f}{g} + f^2} + f \]
By determining \( f \) \& \( g \) from measured levels \( E(v, j) \), \( R_1 \) and \( R_2 \) can be found.

\[ I = \int \rho(R) \, dR = \int dR \sqrt{2 \mu \left[ E - E_{\text{plt}}(R) - \frac{k^2}{2} \right]} = h \left( \frac{\nu}{c} \right) \]

for quantization, \([ I \text{ : action integral } ]\)

(see H. Friedrich book for details)

\[ f(u) = \frac{\sqrt{\frac{\hbar^3}{2 \mu u^2 c}}} \int_0^{u^k} \frac{dv}{\sqrt{u^k - G(v)}} \]

\[ g(u) = \frac{8\pi \sqrt{2\mu c}}{\hbar} \int_0^{u^k} \frac{B(u) \, du}{\sqrt{u^k - G(v)}} \]

with \( E = \frac{T(v, j)}{hc} \cdot G(u) + F(v, j) \)

b) IPA: (Involved Perturbation Approach)

The energy is optimized to agree with measured values (variational approach):

\[ E_{\text{pot}}(R) = E_{\text{pot}}^{(c)}(R) + \Delta E_{\text{pot}}(R) \]

\( R \) initial potential, e.g. RKR

\[ \Rightarrow \Delta E_{v, j} = \langle \Phi^{(c)}_{v, j} | \Delta E_{\text{pot}}(R) | \Phi^{(c)}_{v, j} \rangle \]

Modify \( \Delta E_{\text{pot}} \) until \( \Delta E_{v, j} = E^{(c)}_{v, j} - E^{(c)}_{v, j} \) is acceptable.

More if needed. (not very easy to apply, still need to solve SchEq. at every step).
2.4.6 Long-range interaction

At large separation such that \( R > R_{\text{max}} \) (where \( R_{\text{max}} \) is the uppermost vibrational level \( R_{\text{max}} \)), PKE or IPA cannot be employed.

However, multipole expansion then is applicable, since electron clouds do not overlap.

### Multipole expansion

Consider \( E_{\text{pot}}(P) \) at \( P \) created by \( q_i \) at \( r_i \) far away. We can then expand

\[
E_{\text{pot}}(P) = \frac{q}{4\pi\varepsilon_0 R} + \frac{\rho \cdot \mathbf{r}}{4\pi\varepsilon_0 R^2} + \frac{1}{2} \frac{\sigma}{4\pi\varepsilon_0 R^3} + \cdots
\]

- Monopole
- Dipole
- Quadrupole - higher terms

with

\[
q = \sum q_i, \quad \rho = \sum q_i r_i, \quad \sigma = \sum q_i \left[3(r_i \cdot r_i^2) - r_i^2 \right]
\]

Total charge \( q \), total dipole \( \rho \), total quadrupole \( \sigma \)

**Note:** for neutral atoms \( \sum q_i = 0 \)

if no external field \( \Rightarrow \rho = 0 \) (averaged over time)

- for spherical symmetric charge density \( \Rightarrow \sigma = 0 \)
- \( \Rightarrow E_{\text{pot}}(R) = \sum \frac{C_n}{R^n} \), required \( n > 3 \) for neutral ground state atoms.