Rotation and vibration coupling

To summarize:

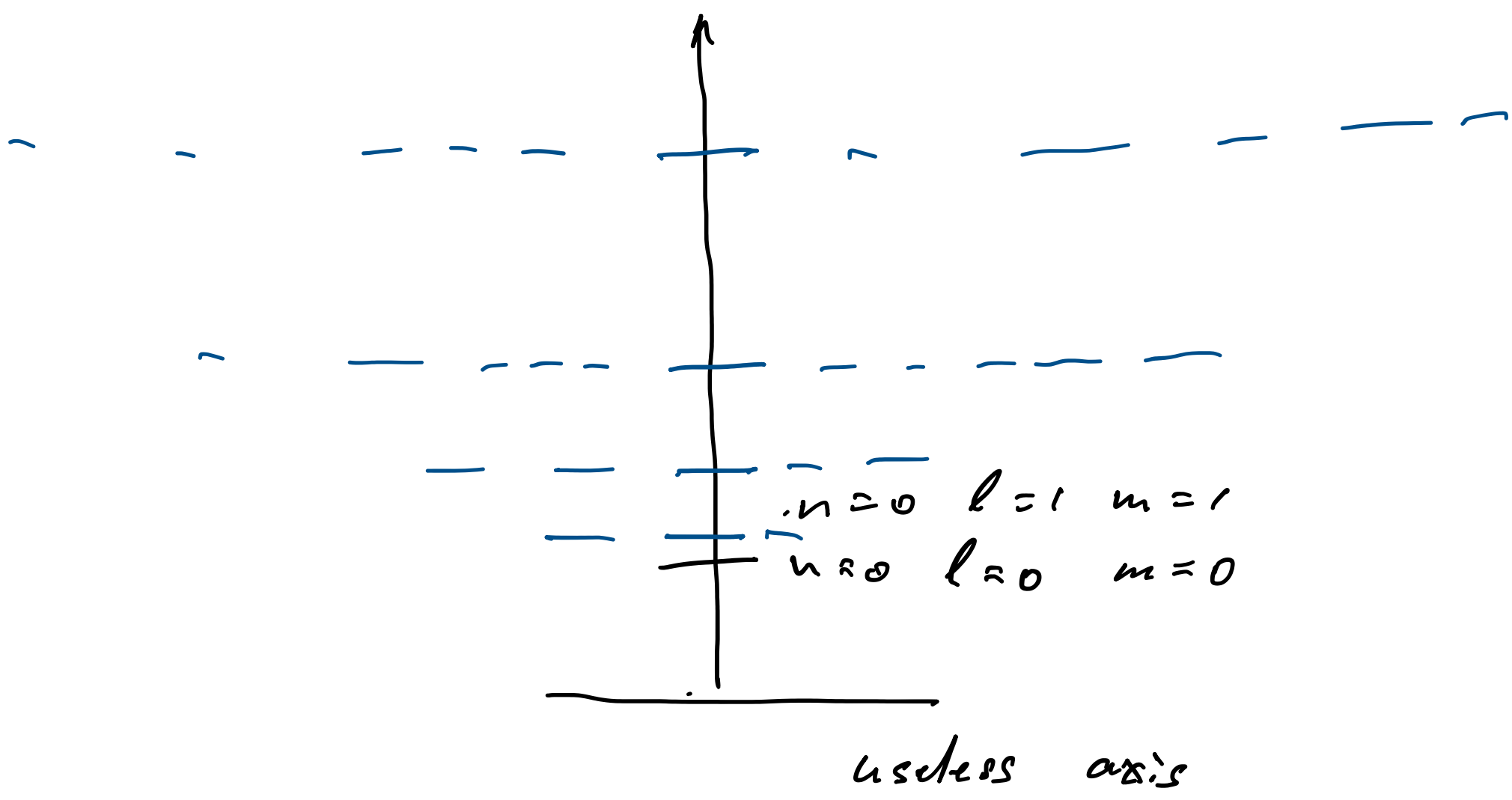
HO: $E_n = \left(n + \frac{1}{2}\right) h\nu_0$

RR: $E_\ell = B_e \ell(\ell+1)$

$$B_e = \frac{h^2}{8\pi^2 r^2 \mu}$$

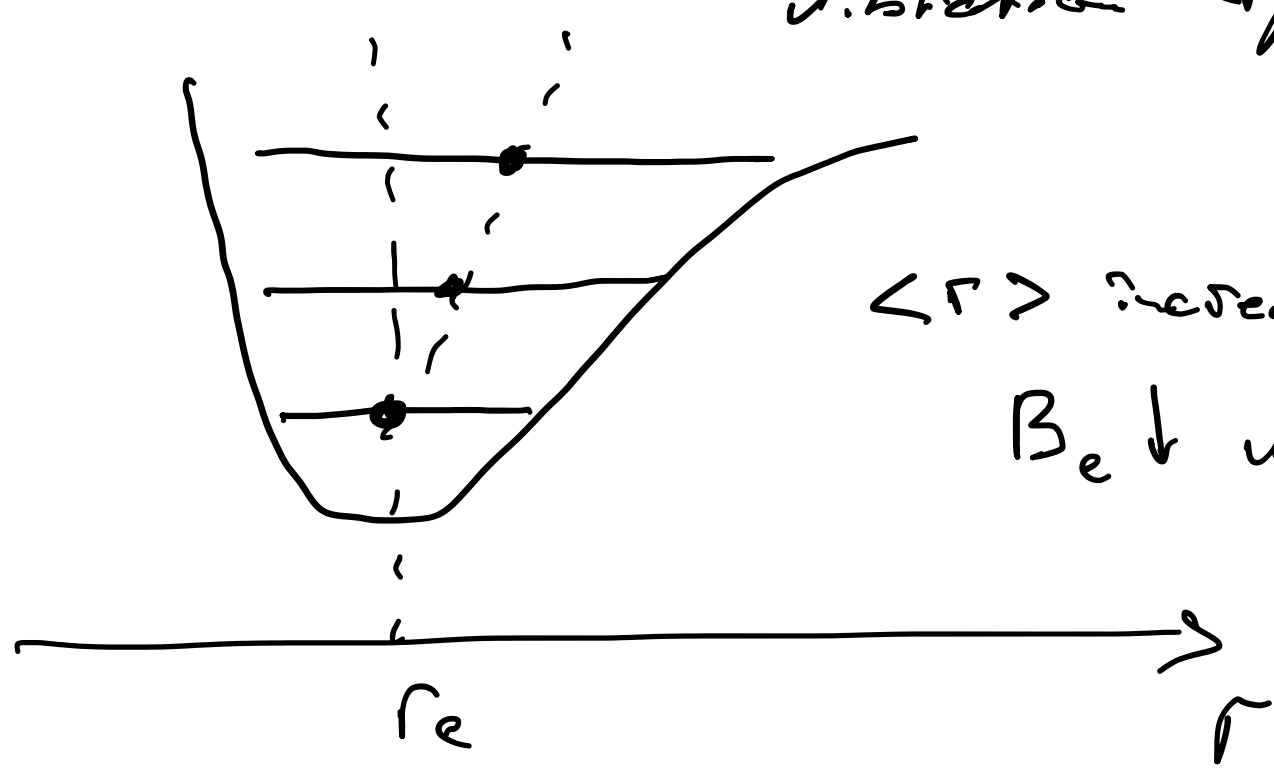
Total energy:

$$E_{n,\ell} = E_n + E_\ell = \left(n + \frac{1}{2}\right) h\nu_0 + B_e \ell(\ell+1)$$



One problem though, B_e will differ if molecule vibrate!

$$E_\ell = \frac{h^2}{8\pi^2 \mu r^2}$$ ← vibration dependent.



$\langle r \rangle$ increase with n

$B_e \downarrow$ with $n \uparrow$

$$B_e' = B_e - \alpha_\ell \left(n + \frac{1}{2}\right)$$

↘ coupling constant

$$\bar{E}_{n,\ell} = \left(n + \frac{1}{2}\right)\nu_0 + B_e \ell(\ell+1) - \alpha_\ell \left(n + \frac{1}{2}\right)\ell(\ell+1)$$