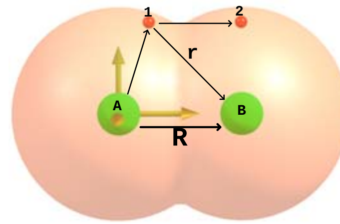
$$\hat{H} = \hat{H}^{e} + \hat{T}$$



$$\hat{T} = (\frac{-\hbar^2}{2M_a}\nabla_a^2) + (\frac{-\hbar^2}{2M_b}\nabla_b^2)$$

$$\hat{H}^{e} = (\frac{-\hbar^2}{2}\sum_{i=1}^{N}\nabla_i^2) + (\sum_{i}^{N} -\frac{Z_a}{|\vec{r}_{ia}|}) + (\sum_{i}^{N} -\frac{Z_b}{|\vec{r}_{ib}|}) + (\sum_{i<j}\frac{1}{|\vec{r}_{ij}|}) + (\frac{Z_a Z_b}{|\vec{R}|})$$

$$\hat{H}\mathbf{\Psi}(\mathbf{r}\,|\,\mathbf{R}) = E\mathbf{\Psi}(\mathbf{r}\,|\,\mathbf{R})$$

$\mathbf{r}$: *electrons* coordinate including spin $\qquad$ $\mathbf{R}$: Nuclie coordinate

$$\hat{H}^{e}\psi_k^e(\mathbf{r}\,|\,\mathbf{R}) = E_k^e\psi_k^e(\mathbf{r}\,|\,\mathbf{R})$$

$\mathbf{\Psi}_{gr}(\mathbf{r}\,|\,\mathbf{R}) = \psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})$ Approx 1, gr : ground electronic state

$\chi_{gr}(\mathbf{R})$ = nuclie motion wave function

$$\langle\psi_{gr}^e\,|\,\psi_{gr}^e\rangle = 1 = \int_{\mathbf{r}}\psi_{gr}^{*,e}\psi_{gr}^e d^n\mathbf{r}$$

$$\hat{H}\mathbf{\Psi}_{gr}(\mathbf{r}\,|\,\mathbf{R}) = \hat{H}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R}) = E\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}\hat{H}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}E\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})(\hat{H}^e + \hat{T})\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = E\chi_{gr}(\mathbf{R})\int_{\mathbf{r}}\psi_{gr}^{*,e}\psi_{gr}^e d^n\mathbf{r}$$

$$\{\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})\hat{H}^e\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}\} + \{\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})(\hat{T})\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}\} = E\chi_{gr}(\mathbf{R})$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})\hat{T}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}\hat{T}\psi_{gr}^e\chi_{gr}d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_a}\nabla_a^2 + \frac{-\hbar^2}{2M_b}\nabla_b^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r}$$

$$= \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_a}\nabla_a^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_b}\nabla_b^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\psi_{gr}^e\nabla_a^2\chi_{gr} + \chi_{gr}\nabla_a^2\psi_{gr}^e + 2\nabla_a\psi_{gr}^e\nabla_a\chi_{gr})\}d^n\mathbf{r}$$

$$+ \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\psi_{gr}^e\nabla_b^2\chi_{gr} + \chi_{gr}\nabla_b^2\psi_{gr}^e + 2\nabla_b\psi_{gr}^e\nabla_b\chi_{gr})\}d^n\mathbf{r}$$

$$= \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\psi_{gr}^e\nabla_a^2\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\psi_{gr}^e\nabla_b^2\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\chi_{gr}\nabla_a^2\psi_{gr}^e)\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\chi_{gr}\nabla_b^2\psi_{gr}^e)\}d^n\mathbf{r}$$

$$+ \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(2\nabla\psi_{gr}^e\nabla_a\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(2\nabla_b\psi_{gr}^e\nabla_b\chi_{gr})\}d^n\mathbf{r}$$

Approx2

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\chi_{gr}\nabla_a^2\psi_{gr}^e)\}d^n\mathbf{r}+\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\chi_{gr}\nabla_b^2\psi_{gr}^e)\}d^n\mathbf{r}+\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(2\nabla\psi_{gr}^e\nabla_a\chi_{gr})\}d^n\mathbf{r}$$

$$+\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(2\nabla_b\psi_{gr}^e\nabla_b\chi_{gr})\}d^n\mathbf{r}=0$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})\hat{T}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}\approx\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\psi_{gr}^e\nabla_a^2\chi_{gr})\}d^n\mathbf{r}+\int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\psi_{gr}^e\nabla_b^2\chi_{gr})\}d^n\mathbf{r}$$

$$=\hat{T}\chi_{gr}(\mathbf{R})$$

$$E_{gr}^e(\mathbf{R})\chi_{gr}(\mathbf{R})+\hat{T}\chi_{gr}(\mathbf{R})=E\chi_{gr}(\mathbf{R})\qquad E=\text{all nuclear motions }=E^{trv}$$

BO - Schrodinger equation of nuclie motion in the charge distribution of ground electronic state

$$\hat{T}\chi_{gr}(\mathbf{R})+E_{gr}^e(\mathbf{R})\chi_{gr}(\mathbf{R})=E^{trv}\chi_{gr}(\mathbf{R})$$

$$\hat{T}\chi(\mathbf{R})+E_{gr}^e(R)\chi(\mathbf{R})=E^{trv}\chi(\mathbf{R})$$

$$\hat{T}=\{\frac{-\hbar^2}{2M_a}(\frac{\partial^2}{\partial x_a^2}+\frac{\partial^2}{\partial y_a^2}+\frac{\partial^2}{\partial z_a^2})+\frac{-\hbar^2}{2M_b}(\frac{\partial^2}{\partial x_b^2}+\frac{\partial^2}{\partial y_b^2}+\frac{\partial^2}{\partial z_b^2})\}\chi(\mathbf{R})$$

Approximations

$$\chi(\mathbf{R})=\chi^t(\mathbf{R}_{cm})\chi^{rv}(\mathbf{R}_{xyz})\quad\text{and}\quad E^{trv}=E^t+E^{rv}$$

Defining $\mathbf{R}_{cm}$ and $\mathbf{R}_{xyz}$

$$M=M_a+M_b\qquad\text{and}\qquad\mu=\frac{M_aM_b}{M_a+M_b}$$

$$X_{cm}=\frac{1}{M}(M_ax_a+M_bx_b)\quad,\quad Y_{cm}=\frac{1}{M}(M_ay_a+M_by_b)\;,\;\; Z_{cm}=\frac{1}{M}(M_az_a+M_bz_b)$$

$$x=x_a-x_b\quad,\quad y=y_a+y_b\quad,\quad z=z_a+z_b$$

$$\hat{T}=\{\frac{-\hbar^2}{2M_a}(\frac{\partial^2}{\partial x_a^2}+\frac{\partial^2}{\partial y_a^2}+\frac{\partial^2}{\partial z_a^2})+\frac{-\hbar^2}{2M_b}(\frac{\partial^2}{\partial x_b^2}+\frac{\partial^2}{\partial y_b^2}+\frac{\partial^2}{\partial z_b^2})\}\chi^t(\mathbf{R}_{cm})\chi^{rv}(\mathbf{R}_{xyz})$$

$$\frac{\partial^2}{\partial x_a^2}\chi^t(\mathbf{R}_{cm})\chi^{rv}(\mathbf{R}_{xyz})=\frac{\partial}{\partial x_a}(\frac{\partial\chi^t\chi^{rv}}{\partial x_a})=\frac{\partial}{\partial x_a}(\chi^{rv}\frac{\partial\chi^t}{\partial x_a}+\chi^t\frac{\partial\chi^{rv}}{\partial x_a})$$

$$\frac{\partial\chi^t}{\partial x_a}=\frac{\partial\chi^t}{\partial X}\frac{\partial X}{\partial x_a}=\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\quad,\quad\frac{\partial\chi^{rv}}{\partial x_a}=\frac{\partial\chi^{rv}}{\partial x}\frac{\partial x}{\partial x_a}=\frac{\partial\chi^{rv}}{\partial x}\quad,\frac{\partial x}{\partial x_a}=1\;,\;\frac{\partial x}{\partial x_b}=-1$$

$$\frac{\partial}{\partial x_a}(\chi^{rv}\frac{\partial\chi^t}{\partial x_a}+\chi^t\frac{\partial\chi^{rv}}{\partial x_a})=\frac{\partial}{\partial x_a}(\chi^{rv}\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}+\chi^t\frac{\partial\chi^{rv}}{\partial x})=\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x_a}+\chi^{rv}\frac{M_a}{M}\frac{\partial}{\partial x_a}(\frac{\partial\chi^t}{\partial X})$$

$$+\frac{\partial\chi^t}{\partial x_a}\frac{\partial\chi^{rv}}{\partial x}+\chi^t\frac{\partial}{\partial x_a}(\frac{\partial\chi^{rv}}{\partial x})=\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}+\chi^{rv}\frac{M_a}{M}\frac{\partial}{\partial X}(\frac{\partial\chi^t}{\partial X})\frac{\partial X}{\partial x_a}+\frac{\partial\chi^t}{\partial X}\frac{\partial X}{\partial x_a}\frac{\partial\chi^{rv}}{\partial x}+\chi^t\frac{\partial}{\partial x}(\frac{\partial\chi^{rv}}{\partial x})\frac{\partial x}{\partial x_a}$$

$$=\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}+\chi^{rv}\frac{M_a^2}{M^2}\frac{\partial^2\chi^t}{\partial X^2}+\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}+\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}=\chi^{rv}\frac{M_a^2}{M^2}\frac{\partial^2\chi^t}{\partial X^2}+\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}+2\frac{M_a}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}$$

$$\frac{\partial^2}{\partial x_b^2}\chi^t(R_{cm})\chi^{rv}(R_{xyz})=\chi^{rv}\frac{M_b^2}{M^2}\frac{\partial^2\chi^t}{\partial X^2}+\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}-2\frac{M_b}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}$$

$$\{\frac{-\hbar^2}{2M_a}(\frac{\partial^2}{\partial x_a^2})+\frac{-\hbar^2}{2M_b}(\frac{\partial^2}{\partial x_b^2})\}\chi^t(R_{cm})\chi^{rv}(R_{xyz})=\chi^{rv}\frac{-\hbar^2M_a}{2M^2}\frac{\partial^2\chi^t}{\partial X^2}+\chi^{rv}\frac{-\hbar^2M_b}{2M^2}\frac{\partial^2\chi^t}{\partial X^2}+\frac{-\hbar^2}{2M_a}\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}$$

$$+\frac{-\hbar^2}{2M_b}\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}-\frac{\hbar^2}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}+\frac{\hbar^2}{M}\frac{\partial\chi^t}{\partial X}\frac{\partial\chi^{rv}}{\partial x}=\frac{-\hbar^2}{M}\chi^{rv}\frac{\partial^2\chi^t}{\partial X^2}+\frac{-\hbar^2}{2\mu}\chi^t\frac{\partial^2\chi^{rv}}{\partial x^2}$$

$$\hat{T}\chi^t(\mathbf{R}_{cm})\chi^{rv}(\mathbf{R}_{xyz})=\frac{-\hbar^2}{M}\chi^{rv}(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2})\chi^t+\frac{-\hbar^2}{2\mu}\chi^t(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\chi^{rv}$$

$\hat{T}\chi(\mathbf{R})+E_{gr}^e(\mathbf{R})\chi(\mathbf{R})=E^{trv}\chi(\mathbf{R})$ master equation

$$\frac{-\hbar^2}{M}\chi^{rv}(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2})\chi^t+\frac{-\hbar^2}{2\mu}\chi^t(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\chi^{rv}+E_{gr}^e(R)\chi^t\chi^{rv}=(E^t+E^{rv})\chi^t\chi^{rv}$$

$$\{\frac{-\hbar^2}{M}\chi^{rv}(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2})\chi^t-E^t\chi^t\chi^{rv}\}+\{\frac{-\hbar^2}{2\mu}\chi^t(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\chi^{rv}+E_{gr}^e(R)\chi^t\chi^{rv}-E^{rv}\chi^t\chi^{rv}\}=0$$

$\frac{-\hbar^2}{M}(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2})\chi^t-E^t\chi^t=0$ free particle motion

$\frac{-\hbar^2}{2\mu}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\chi^{rv}+E_{gr}^e(\mathbf{R})\chi^{rv}-E^{rv}\chi^{rv}=0$ Viration - Rotation of molecule at ground electronic state

$$\frac{-\hbar^2}{2\mu}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\chi^{rv}+E_{gr}^e(\mathbf{R})\chi^{rv}-E^{rv}\chi^{rv}=0$$

Transfering ∇^2 to spherical polar coordinates

$R=\sqrt{x^2+y^2+z^2}$, $x=R\sin\theta\cos\phi$, $y=R\sin\theta\sin\phi$, $z=R\cos\theta$

$\chi^{rv}=\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)$

$$\frac{-\hbar^2}{2\mu R^2}\{\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)}{\partial R})+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)}{\partial\theta})+\frac{1}{\sin^2\theta}\frac{\partial^2\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)}{\partial\phi^2}\}$$

$$+\{E_{gr}^e(R)-E^{rv}\}\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)=0$$

$$\frac{-\hbar^2}{2\mu R^2}\{\chi_\theta(\theta)\chi_\phi(\phi)\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\chi_R(R)\chi_\phi(\phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})+\chi_R(R)\chi_\theta(\theta)\frac{1}{\sin^2\theta}\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}\}$$

$$+\{E_{gr}^e(R)-E^{rv}\}\chi_R(R)\chi_\theta(\theta)\chi_\phi(\phi)=0$$

$$\frac{-\hbar^2}{2\mu R^2}\{\frac{1}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\frac{1}{\chi_\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})+\frac{1}{\chi_\phi(\phi)\sin^2\theta}\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}\}+(E^e_{gr}(R)-E^{rv})=0$$

$$\{\frac{1}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\frac{1}{\chi_\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})+\frac{1}{\chi_\phi(\phi)\sin^2\theta}\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}\}+\{(\frac{-2\mu R^2}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}=0$$

$$\{\frac{\sin^2\theta}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\frac{\sin\theta}{\chi_\theta(\theta)}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})+\frac{1}{\chi_\phi(\phi)}\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}\}+\{(\frac{-2\mu R^2\sin^2\theta}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}=0$$

$$\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}=-m^2\chi_\phi(\phi)\Rightarrow\frac{1}{\chi_\phi(\phi)}\frac{\partial^2\chi_\phi(\phi)}{\partial\phi^2}=-m^2$$

$$\{\frac{\sin^2\theta}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\frac{\sin\theta}{\chi_\theta(\theta)}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})-m^2\}+\{(\frac{-2\mu R^2\sin^2\theta}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}=0$$

$$\{\frac{1}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\frac{1}{\chi_\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})-\frac{m^2}{\sin^2\theta}\}+\{(\frac{-2\mu R^2}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}=0$$

$$\{\frac{1}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\{(\frac{-2\mu R^2}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}+\{\frac{1}{\chi_\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\chi_\theta(\theta)}{\partial\theta})-\frac{m^2}{\sin^2\theta}\}=0$$

$$\frac{1}{\chi_R(R)}\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})+\{(\frac{-2\mu R^2}{\hbar^2})(E^e_{gr}(R)-E^{rv})\}+\{J(J+1)\}=0$$

$J=0,1,2,3,\ldots$

$$\frac{\partial}{\partial R}(R^2\frac{\partial\chi_R(R)}{\partial R})=2R\frac{\partial\chi_R(R)}{\partial R}+R^2\frac{\partial^2\chi_R(R)}{\partial R^2}$$

$$\frac{1}{\chi_R(R)}(2R\frac{\partial\chi_R(R)}{\partial R}+R^2\frac{\partial^2\chi_R(R)}{\partial R^2})+(\frac{-2\mu R^2}{\hbar^2})(E^e_{gr}(R)-E^{rv})+J(J+1)=0$$

$$\frac{1}{\chi_R(R)}(\frac{2}{R}\frac{\partial\chi_R(R)}{\partial R}+\frac{\partial^2\chi_R(R)}{\partial R^2})+(\frac{-2\mu}{\hbar^2})(E^e_{gr}(R)-E^{rv})+\frac{J(J+1)}{R^2}=0$$

$$\chi_R(R)=\frac{P_R(R)}{R},\quad\frac{\partial\chi_R(R)}{\partial R}=-\frac{1}{R^2}P_R(R)+\frac{1}{R}\frac{\partial P_R(R)}{\partial R}$$

$$\frac{\partial^2\chi_R(R)}{\partial R^2}=\frac{2}{R^3}P_R(R)-\frac{1}{R^2}\frac{\partial P_R(R)}{\partial R}-\frac{1}{R^2}\frac{\partial P_R(R)}{\partial R}+\frac{1}{R}\frac{\partial^2P_R(R)}{\partial R^2}$$

$$\frac{R}{P_R(R)}(-\frac{2}{R^3}P_R(R)+\frac{2}{R^2}\frac{\partial P_R(R)}{\partial R}+\frac{2}{R^3}P_R(R)-\frac{2}{R^2}\frac{\partial P_R(R)}{\partial R}+\frac{1}{R}\frac{\partial^2P_R(R)}{\partial R^2})+(\frac{-2\mu}{\hbar^2})(E^e_{gr}(R)-E^{rv})+\frac{J(J+1)}{R^2}=0$$

$$\frac{1}{P_R(R)}\frac{\partial^2P_R(R)}{\partial R^2}+(\frac{-2\mu}{\hbar^2})(E^e_{gr}(R)-E^{rv})+\frac{J(J+1)}{R^2}=0$$

$$\frac{\partial^2P_R(R)}{\partial R^2}+\{\frac{-2\mu}{\hbar^2}E^e_{gr}(R)+\frac{J(J+1)}{R^2}+\}P_R(R)+\frac{2\mu}{\hbar^2}E^{rv}=0$$

$J=0$ are the vibrational levels without the effect of rotation

$J\neq0$ coupling between rotation and vibration