Transformace soustav – pokračování

- V malé vzdálenosti jsou dobrá kv. čísla $(JMl\Lambda)$
- V laboratorní soustavě – " – $(JMlj)$
- Obě soustavy spojuje unitární transformace $\cancel{\Phi^{JM}_{lj} = \sum_\Lambda X^{JM}_{l\Lambda} \cdot U^{JM}_{\Lambda j}(l)}$

$$X^{JM}_{l\Lambda}(\hat r, \hat R) = \sum_j \Phi^{JM}_{lj}(\hat r, \hat R)\, U^{JM}_{j\Lambda}(l)$$

$$\boxed{U^{JM}_{j\Lambda}(l) = \left(\frac{2j+1}{2J+1}\right)^{1/2} (l\, j\, J \mid \Lambda\, 0\, \Lambda)}$$

člen

$$\langle X^{JM}_{l\Lambda} | H^{(rot)} | X^{JM}_{l\Lambda'} \rangle = B \sum_j U^{JM}_{\Lambda j}(l)\, j(j+1)\, U^{JM}_{j\Lambda}(l)$$

- Asymptotika v laboratorní soustavě a existence více řešení

$$u^{JM}_{lj, l_0 j_0}(r) \longrightarrow \delta_{ll_0}\delta_{jj_0}\, \hat j_{l_0}(k_0 r) - \left(\frac{k_{j_0}}{k_j}\right)^{1/2} K_{lj, l_0 j_0}\, \hat n_l(k_j r)$$

$$\longrightarrow \delta_{ll_0}\delta_{jj_0}\, \hat j_{l_0}(k_0 r) + \left(\frac{k_{j_0}}{k_j}\right)^{1/2} T_{lj, l_0 j_0}\, e^{i(k_j r - \frac{l\pi}{2} - \frac{\pi}{4})}$$

$$\hat h^+_l(k_j r)$$

- Asymptotika v soustavě molekuly

$$g^{JM}_{l\Lambda, l_0\Lambda_0}(r) \longrightarrow \delta_{ll_0}\delta_{\Lambda\Lambda_0}\, \hat j_{l_0}(k_0 r) - \left(\frac{k_{\Lambda_0}}{k_\Lambda}\right)^{1/2} K_{l\Lambda, l_0\Lambda_0}\, \hat n_l(k_\Lambda r)$$

$$\longrightarrow \quad \dots \quad T_{l\Lambda, l_0\Lambda_0} \dots$$

$$\boxed{T^{JM}_{lj, l_0 j_0} = \sum_{\Lambda\Lambda_0} U^{JM}_{j\Lambda}\, T^{JM}_{l\Lambda, l_0\Lambda_0}\, U^{JM}_{l_0 \Lambda_0 j_0}}$$

Asymptotika S-matice doplnit

FT S-matice jako limitní případ.

- Rovnici BODY1 násobíme zleva a sumujeme: $\sum_v \chi_v(R)$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-E\right]h^{JM}_{l\Lambda}(r,R)+B\sum_{\Lambda' j}U^{JM}_{\Lambda j}j(1+j)\,U^{JM}_{j\Lambda'}(l)\,h^{JM}_{l\Lambda'}(r,R)\quad+A\quad+B\quad=0$$

(A) $\sum_v \omega(v+1/2)\,\chi_v(R)\,g^{JM}_{l\Lambda v}(r)=\sum_v \omega(v+\frac{1}{2})\chi_v(R)\int_0^\infty dR'\,\chi_v(R')\,h^{JM}_{l\Lambda}(r,R)=$

$$=\int_0^\infty dR'\,\underbrace{\left[\sum_v \chi_v(R)\,\omega(v+\tfrac{1}{2})\,\chi_v(R')\right]}\,h^{JM}_{l\Lambda}(r,R')$$

$H_v=\sum_v|\chi_v\rangle\,\varepsilon_v\,\langle\chi_v|$ ... spektrální rozklad vibračního hamiltoniánu v R-reprezentaci

(B)

$$\sum_{v v' l'}\chi_v(R)\langle X^{JM}_{l\Lambda}(\hat r,\hat R)\,\chi_v(R')\,|\,V_{int}(\vec r,\hat R,R)\,|\,X^{JM}_{l'\Lambda}\,\chi_{v'}(R)\rangle\,g^{JM}_{l'\Lambda v'}(r)=$$

$$=\sum_{l'}\langle X^{JM}_{l\Lambda}(\hat r,\hat R)\,|\,V_{int}(\vec r,\hat R,R)\,|\,X^{JM}_{l'\Lambda}(R)\rangle\,h^{JM}_{l'\Lambda}(r,R)$$

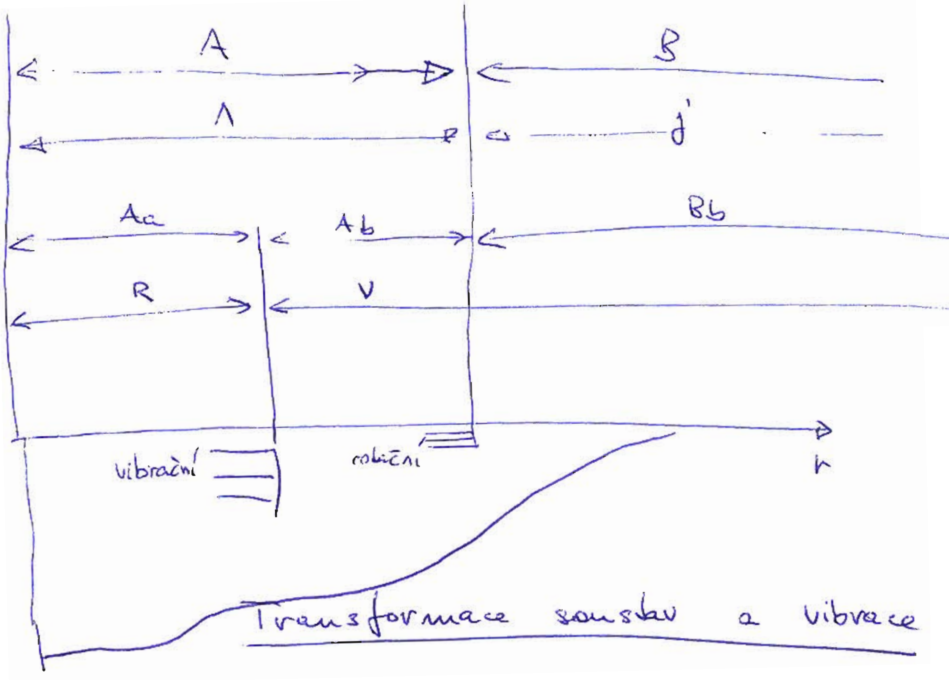
- Paralela s BODY v rotacích. - diskuse obrázku Ab, Aa, ...

kanálová energie $\underline{\frac{1}{2}k^2_{jv}=E-B_j(j+1)-\omega(v+1/2)}$

Obecněji o transformaci soustav

- přechod ze soustavy s kv. čísly $A,B,C\longrightarrow A,B,D$, kde operátory příslušné C a D nekomutují
- v rotační FT: ~~A~~, (Λ,j)

  vibrační FT: (R,v)
- Rydbergovy stavy H_2:



Transformace soustav a vibrace

$$\left[\hat{T}_e + H^{(rot)}(\hat{R}) + H^{(vib)}(R) + V_{int}(\vec{r},\vec{R}) - E\right]\psi(\vec{r},\vec{R}) = 0$$

LAB

$$\psi^{JM}(\vec{r},\vec{R}) = \frac{1}{r}\sum_{\ell j v} u^{JM}_{\ell j v}(r)\,\chi_v(R)\,\Phi^{JM}_{\ell j}(\hat{r},\hat{R})$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + B\,j(j+1) + \omega\left(v+\tfrac{1}{2}\right) - E\right]u^{JM}_{\ell j v}(r) + \sum_{\ell' j' v'}\langle \Phi^{JM}_{\ell j}\chi_v | V(\vec{r},\vec{R}) | \Phi^{JM}_{\ell' j'}\chi_{v'}\rangle u^{JM}_{\ell' j' v'}(r) = 0$$

BODY1:

$$\psi^{JM}(\vec{r},\vec{R}) = \frac{1}{r}\sum_{\ell \Lambda v} g^{JM}_{\ell\Lambda v}(r)\,\chi_v(R)\,\chi^{J\ell}_{\ell\Lambda}(\hat{r},\hat{R})$$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + \omega\left(v+\tfrac{1}{2}\right) - E\right]g^{JM}_{\ell\Lambda v}(r) + B\sum_{\Lambda' j} U^{JM}_{\Lambda j}(\ell)\,j(j+1)\,U^{JM}_{j\Lambda'}(\ell)\,g^{JM}_{\ell\Lambda v}(r) + \sum_{\ell' v'}\langle \chi^{JM}_{\ell\Lambda}\chi_v | V_{int} | \chi^{JM}_{\ell'\Lambda'}\chi_{v'}\rangle g^{JM}_{\ell\Lambda' v'} = 0$$

- Vznik nové transformace soustav: kv. číslo R $\longrightarrow$ kv. číslo V
- Roli unitární transformace hrají matice $U_{RV} = \chi_v(R)$
- Zavedeme funkce $h^{JM}_{\ell\Lambda}(r,R) = \sum_v g^{JM}_{\ell\Lambda v}(r)\,\chi_v(R)$

$$g^{JM}_{\ell\Lambda v}(r) = \int_0^\infty dR\,\chi_v(R)\,h^{JM}_{\ell\Lambda}(r,R)$$

- Ortogonalita a úplnost:

$$\int_0^\infty dR\,\chi_v(R)\,\chi_{v'}(R) = \delta_{vv'}$$

$$\sum_{v=0}^\infty \chi_v(R)\,\chi_v(R') = \delta(R-R')$$