① 12/12/1999

$\langle x | k_x \rangle = \frac{1}{\sqrt{2\pi}} e^{i k_x \cdot x}$

$\hat{I}_x = \int | k_x \rangle \, dk_x \, \langle k_x |$

$| \underline{k} \rangle = | k_x \rangle | k_y \rangle | k_z \rangle$

$\hat{I} = \iiint \hat{I}_x \cdot \hat{I}_y \hat{I}_z = \iiint | \underline{k} \rangle \, dk_x \, dk_y \, dk_z \, \langle \underline{k} | = \iiint | \underline{k} \rangle \, d\underline{k} \, \langle \underline{k} |$

$k = | \underline{k} |$

$\hat{k} = (\theta_k, \phi_k)$

$\underline{r} = (x, y, z) \qquad | \underline{r} \rangle = | x \rangle | y \rangle | z \rangle$

$\langle \underline{r} | \underline{k} \rangle = \frac{1}{\sqrt{2\pi}} e^{i k_x \cdot x} \frac{1}{\sqrt{2\pi}} e^{i k_y \cdot y} \frac{1}{\sqrt{2\pi}} e^{i k_z \cdot z} = \frac{1}{(2\pi)^{3/2}} e^{i \underline{k} \cdot \underline{r}}$

$d\underline{k} = k^2 \, dk \, d\hat{k} \qquad [d\hat{k} = d\cos\theta_k \, d\phi_k]$

$E = \frac{\hbar^2 k^2}{2\mu} + \varepsilon_{\underline{n}} = E_n + \varepsilon_n$

$\frac{dE}{dk} = \frac{2 k \hbar^2}{2\mu} = \frac{\hbar^2}{\mu} k$

$\frac{\mu}{\hbar^2} dE = k \, dk \implies k^2 dk = \frac{k \mu}{\hbar^2} dE$

$d\underline{k} = k^2 \, dk \, d\hat{k} = \frac{k\mu}{\hbar^2} dE \, d\hat{k}$

$\langle \underline{r} | \hat{k} k \rangle = \frac{1}{(2\pi)^{3/2}} e^{i \underline{k} \cdot \underline{r}}$

$\hat{I} = \iint | \hat{k} k \rangle k^2 \, dk \, d\hat{k} \, \langle \hat{k} k |$

$= \iint | \hat{k} k \rangle \frac{k \cdot \mu}{\hbar^2} dE \, d\hat{k} \, \langle \hat{k} k |$

$| \hat{k} E \rangle = \frac{\sqrt{k\mu}}{\hbar} | \hat{k} k \rangle \implies \hat{I} = \iint | \hat{k} E \rangle \, dE \, d\hat{k} \, \langle \hat{k} E |$

$\langle \underline{r} | \hat{k} E \rangle = \left(\frac{k\mu}{\hbar^2} \right)^{1/2} \left(\frac{1}{(2\pi)^3} \right)^{1/2} e^{i \underline{k} \cdot \underline{r}} = \left[\frac{k\mu}{\hbar^2 (2\pi)^3} \right]^{1/2} e^{i \underline{k} \cdot \underline{r}}$

$e^{i \underline{k} \cdot \underline{r}} = 4\pi \sum_{\substack{l=0 \\ m_l = -l}}^{\infty} i^l j_l(k r) \, Y_{lm}(\theta_r, \phi_r) \, Y^*_{lm}(\theta_k, \phi_k)$

$j_l(k \cdot r)$ spherical Bessel functions of the first kind A&S 10.1.1

$j_0(z) = \frac{\sin z}{z}$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}\cdot R + \frac{\hat{l}^2}{2\mu R^2} + \underbrace{\hat{T}_0(\underline{q}) + V_0(\underline{q})}_{H_0(\underline{q})} + \Delta V(R,\underline{q})$$

Skip 2–8

$$V(R,\underline{q}) = V_0(\underline{q}) + \Delta V(R,\underline{q})$$

$$\begin{cases} V_0(\underline{q}) \equiv \lim_{R\to\infty} V(R,\underline{q}) \\ \Delta V(R,\underline{q}) \equiv V(R,\underline{q}) - V_0(\underline{q}) \end{cases}$$

$$\hat{H}_0(\underline{q}) \equiv \hat{T}_0(\underline{q}) + V_0(\underline{q})$$

$$\hat{T}_R = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R$$

$$\hat{H}_0(R,\underline{q}) = \hat{T}_R + \hat{H}_0(\underline{q})$$

Channel eigen functions

$$[\hat{T}_0(\underline{q}) + V_0(\underline{q})]\,|\underline{n}\rangle = \varepsilon_{\underline{n}}\,|\underline{n}\rangle$$

Energy normalized free wave in direction $\hat{k}$, state $|\underline{n}\rangle$

$$\langle R\underline{q}\,|\,\hat{k}E\underline{n}\rangle = \left[\frac{k_n\mu}{\hbar^2(2\pi)^3}\right]^{1/2} e^{i\underline{k}_n\cdot\underline{R}}\,\langle\underline{q}\,|\,\underline{n}\rangle$$

$$\hat{T}_R\,|\hat{k}E\underline{n}\rangle = E_n\,|\hat{k}E\underline{n}\rangle \qquad E_n \equiv E - \varepsilon_n\ ; = \frac{\hbar^2 k_n^2}{2\mu}$$

$$\hat{H}_0(\underline{q})\,|\hat{k}E\underline{n}\rangle = \varepsilon_n\,|\hat{k}E\underline{n}\rangle$$

$$[\hat{T}_R + \hat{H}_0(\underline{q})]\,|\hat{k}E\underline{n}\rangle = E\,|\hat{k}E\underline{n}\rangle$$

Note
$$\begin{cases} \hat{I} = \sum_{\underline{n}} \iiint d\hat{k}\,dE\ |\hat{k}E\underline{n}\rangle\langle\hat{k}E\underline{n}| \qquad [\rho(E_n) \equiv 1] \\ \langle\hat{k}E\underline{n}\,|\,\hat{k}'E'\underline{n}'\rangle = \delta_{\hat{k}\hat{k}'}\,\delta_{EE'}\,\delta_{\underline{n}\underline{n}'} \end{cases}$$

Partial wave expansion

out IN

$$e^{i\underline{k}\cdot\underline{R}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{i^l}{2i}\left[i h_l^{(1)}(k\cdot R) + i h_l^{(2)}(k\cdot R)\right]\langle\hat{R}\,|\,lm\rangle\,Y^*_{lm}(\theta_k,\phi_k)$$

Asymptotically

$$i\cdot z\,h_l^{(1)}(z) \simeq e^{i(z - l\frac{\pi}{2})} \qquad \text{out} = \oplus v$$

$$i\,z\cdot h_l^{(2)}(z) \simeq -e^{-i(z-l\frac{\pi}{2})} \qquad \text{in} = \ominus u \qquad u = v^*$$

Radial flux

$$j = \frac{\hbar}{\mu}\,\mathrm{Im}[\psi^*\nabla\psi]$$

$$h_l^{(1)}(k\cdot R) \qquad j_R = \frac{\hbar k}{\mu}$$

$$h_l^{(2)}(k\cdot R) \qquad j_R = -\frac{\hbar k}{\mu}$$

$$\cancel{v_l(k\cdot R) = i\sqrt{\frac{\mu k}{\hbar k}}\,k\cdot R\,h_l^{(1)}(k\cdot R)}$$

$$\begin{cases} u \simeq e^{-ix} = \cos - i\sin \\ \quad = -G - iF \\ V = u^* = e^{ix} = -G + iF \end{cases}$$

$$\cancel{v_l(z) \equiv v_l(k\cdot R)} \equiv \left[\frac{\mu}{\hbar k}\right]^{1/2} i\,k\cdot R\,h_l^{(1)}(k\cdot R)$$

$\cancel{v_{l,k}(k\cdot R)}$

~~Uncoupled~~ Full solution

$$\hat{H}\,|\hat{k}E\,\underline{n}^-\rangle = E\,|\hat{k}E\,\underline{n}^-\rangle \quad \left.\right\} \quad \text{By def the same } \underline{\underline{\text{out}}}\text{going part}$$

$$H_0\,|\hat{k}E\,\underline{n}\rangle = E\,|\hat{k}E\,\underline{n}\rangle$$

Photo dissociation cross section

$$\sigma(\hat{k}E\,\underline{n}\,|\,i) = \frac{4\pi^2\omega}{c}\,|\langle \hat{k}E\,\underline{n}^-|\,\hat{e}\cdot\underline{\mu}\,|i\rangle|^2\,\rho(E) \qquad [\rho(E)=1]$$

-77.9

Uncoupled, space fixed

$$|\Psi(R,\hat{R},\underline{q})\rangle = \sum_{\underline{n}\,\ell\,m_\ell} |\underline{n}\rangle\,|\ell m_\ell\rangle\,\frac{1}{R}\,f_{\underline{n},\ell m_\ell}(R)$$

$$(H-E)|\Psi\rangle = 0$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{\ell}^2}{2\mu R^2} + H_0(q) + \Delta V(R,q) - E\right]\sum_{\underline{n}\,\ell m_\ell} |\underline{n}\rangle|\ell m_\ell\rangle\,\frac{1}{R}f_{\underline{n},\ell m_\ell}(R) = 0$$

multiply with $-\frac{2\mu}{\hbar^2}\cdot R$

$$\left\{\frac{\partial^2}{\partial R^2} - \frac{\hat{\ell}^2}{\hbar^2 R^2} - \frac{2\mu}{\hbar^2}\left[H_0 + \Delta V(R,q) - E\right]\right\}\sum_{\underline{n}\,\ell m_\ell} |\underline{n}\rangle\,|\ell m_\ell\rangle\,f_{\underline{n},\ell m_\ell}(R) = 0$$

$\langle \underline{n}'|\langle \ell' m_\ell'|$

$$W_{\underline{n}'\ell' m_\ell';\,\underline{n}\,\ell m_\ell}(R) \equiv \langle \underline{n}'\ell' m_\ell'|\,\frac{\hat{\ell}^2}{\hbar^2 R^2} + \frac{2\mu}{\hbar^2}(H_0 + \Delta V) - \frac{2\mu E}{\hbar^2}\,|\underline{n}\,\ell m_\ell\rangle$$

$$= \left[\frac{\ell(\ell+1)}{R^2} - k_{\underline{n}}^2\right]\delta_{\underline{n}',\underline{n}}\,\delta_{\ell',\ell}\,\delta_{m_\ell',m_\ell} + \frac{2\mu}{\hbar^2}\langle \underline{n}'\ell' m_\ell'|\,\Delta V(R,\underline{q})\,|\underline{n}\,\ell m_\ell\rangle_{\underline{q}}$$

$$\sum_{\underline{n}\,\ell m_\ell} f''_{\underline{n}\,\ell m_\ell}(R)\,\delta_{\underline{n}'\ell' m_\ell';\,\underline{n}\,\ell m_\ell} - W_{\underline{n}'\ell' m_\ell';\,\underline{n}\,\ell m_\ell}(R)\,f_{\underline{n}\,\ell m_\ell}(R)$$

$$\underline{f}''(R) = \underline{W}(R)\,\underline{f}(R)$$

Boundary conditions

$h_\ell^{(1)}(z) = j_\ell(z) + i y_\ell(z)$ (11)

$h_\ell^{(2)}(z) = j_\ell(z) - i y_\ell(z)$

Define flux normalized in and out going waves

out

$$\frac{v_{\underline{n}\,l m_\ell}(R)}{R} \equiv i h_\ell^{(1)}(k_{\underline{n}} \cdot R) \left[\frac{\mu k_n}{\hbar}\right]^{1/2}$$

out

in

$$\frac{u_{\underline{n}\,l m_\ell}(R)}{R} \equiv -i h_\ell^{(2)}(k_{\underline{n}} \cdot R) \left[\frac{\mu k_n}{\hbar}\right]^{1/2}$$

def

in

Asymptotically

$$v_{\underline{n}\,l m_\ell}(R) \cong i (k_{\underline{n}} \cdot R) h_\ell^{(1)}(k_{\underline{n}} \cdot R) \left[\frac{\mu}{\hbar k_{\underline{n}}}\right]^{1/2}$$

$$= e^{i(k_{\underline{n}} \cdot R - \ell \frac{\pi}{2})} \left[\frac{\mu}{\hbar k_{\underline{n}}}\right]^{1/2} \qquad \underline{\text{Flux} = +1}$$

out

$$u_{\underline{n}\,l m_\ell}(R) \cong -i (k_{\underline{n}} \cdot R) h_\ell^{(2)}(k_{\underline{n}} \cdot R) \left[\frac{\mu}{\hbar k_{\underline{n}}}\right]^{1/2}$$

$$= e^{-i(k_{\underline{n}} \cdot R - \ell \frac{\pi}{2})} \left[\frac{\mu}{\hbar k_{\underline{n}}}\right]^{1/2} \qquad \underline{\text{Flux} = -1}$$

in

large R

out — INCOMING

$$\Psi^{\underline{n}\,l m_\ell}(R) \cong |\underline{n}\rangle \frac{v_{\underline{n},l m_\ell}(R)}{R} - \sum_{\underline{n}' l' m_\ell'} |\underline{n}'\rangle \frac{u_{\underline{n}' l' m_\ell'}(R)}{R} S^*_{\underline{n}' l' m_\ell';\,\underline{n}\,l m_\ell}$$

$$|\Psi^{\underline{n}\,l m_\ell}\rangle \equiv \sum_{\underline{n}' l' m_\ell'} |\underline{n}'\rangle |\ell' m_\ell'\rangle \frac{1}{R} f^{\underline{n}\,l m_\ell}_{\underline{n}' l' m_\ell'}(R)$$

where

out — in

$$f^{\underline{n}\,l m_\ell}_{\underline{n}' l' m_\ell'}(R) \cong v_{\underline{n}\,l m_\ell}(R)\, \delta_{\underline{n}'\underline{n}}\, \delta_{l' l}\, \delta_{m_\ell' m_\ell} - u_{\underline{n}' l' m_\ell'}(R)\, S^*_{\underline{n}' l' m_\ell';\,\underline{n}\,l m_\ell}$$

$$|\hat{k} E^- \underline{n}\rangle = \left[\frac{k_n \mu}{\hbar^2 (2\pi)^3}\right]^{1/2} 4\pi \sum_{l=0}^{\infty} \sum_{m_\ell=-l}^{l} \frac{i^{l}}{2i} |\Psi^{\underline{n}\,l m_\ell}\rangle \left[\frac{\hbar}{\mu k_n}\right]^{1/2} Y^*_{l m_\ell}(\theta_k \phi_k)$$

Verify asymptotic outgoing part

$$|\Psi^{\underline{n}\,l m_\ell}\rangle \left[\frac{\hbar}{\mu k_n}\right]^{1/2} \cong \frac{v_{\underline{n}\,l m_\ell}(R)}{R} \left[\frac{\hbar}{\mu k_n}\right]^{1/2} = i h_\ell^{(1)}(k_{\underline{n}} \cdot R)$$

Simplify

$$\left[\frac{k_n \mu}{\hbar^2 (2\pi)^3}\right]^{1/2} \cdot 4\pi \cdot \left[\frac{\hbar}{\mu k_n}\right]^{1/2} \frac{1}{2} = \frac{1}{\sqrt{2\pi}\,\hbar}$$

[NOV 2005]

$$|\hat{k} E^- \underline{n}\rangle = \frac{1}{\sqrt{2\pi\hbar}} \sum_{l=0}^{\infty} \sum_{m_\ell=-l}^{l} i^{l-1} |\Psi^{\underline{n}\,l m_\ell}\rangle Y^*_{l m_\ell}(\theta_k, \phi_k)$$

NOV 2005 (Zie 16/5/2000)

Photodissociation cross section

$$\sigma(\hat{k} E n | i) = \frac{4\pi^2\omega}{c} \left| \langle \hat{k} E^- n | \hat{e}\cdot\mu | i \rangle \right|^2$$

$$\langle \hat{k} E^- n | \hat{e}\cdot\mu | i \rangle = \frac{1}{\sqrt{2\pi}} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} i^{-l+1} Y_{l m_l}(\theta_k, \phi_k) \underbrace{\langle \Psi^{n l m_l} | \hat{e}\cdot\mu | i \rangle}_{M_{n l m_l; i}}$$

$$\sigma = \frac{4\pi^2\omega}{c} \langle \hat{k} E^- n | \hat{e}\cdot\mu | i \rangle^* \langle \hat{k} E^- n | \hat{e}\cdot\mu | i \rangle$$

$$= \frac{2\pi\omega}{c} \sum_{l l' m_l m_l'} i^{+l-1} i^{-l'+1} Y^*_{l m_l}(\theta_k \phi_k) Y_{l' m_l'}(\theta_k \phi_k) M^*_{n l m_l; i} M_{n l' m_l'; i}$$

$$= \frac{2\pi\omega}{c} \sum_{l l' m_l m_l'} i^{l-l'} Y^*_{l m_l}(\theta_k \phi_k) Y_{l' m_l'}(\theta_k \phi_k) M^*_{n l m_l; i} M_{n l' m_l'; i}$$

$$\sigma_{tot} = \iint \sigma(\hat{k} E n | i)\, d\cos\theta_k\, d\phi_k = \frac{2\pi\omega}{c} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \left| M_{n l m_l; i} \right|^2$$

Coupled

$$|(jl)JM\rangle = \sum_{m_j m_l} |j m_j\rangle |l m_l\rangle \langle j m_j l m_l | J M\rangle$$

$$|\Psi\rangle = \sum_{jlJM} \boxed{|(jl)JM\rangle} \frac{1}{R} f_{jlJM}(R)$$

$$(H-E)|\Psi\rangle = 0 \qquad H_0 |(jl)JM\rangle = \varepsilon_j |(jl)JM\rangle$$

$$\underline{f}''(R) = W(R)\underline{f}(R)$$

$$W_{j'l'J'M'; jlJM}(R) = \langle (j'l')J'M' | \frac{\hat{l}^2}{\hbar^2 R^2} + \frac{2\mu}{\hbar^2}(H_0 - E) + \frac{2\mu}{\hbar^2} \Delta V(R;q) | (jl)JM\rangle$$

$$= W^J_{j'l'; jl}(R)\, \delta_{J'J}\, \delta_{M'M}$$

$$\hat{l}^2 |(jl)JM\rangle = l^2 |(jl)JM\rangle$$

$$H_0 |(jl)JM\rangle = \varepsilon_j |(jl)JM\rangle$$

$\boxed{SF}$ (13)

$$W^{J}_{j'l';jl}(R) = \left[\frac{l(l+1)}{\hbar^2} - k_j^2\right]\delta_{j'j}\delta_{l'l} + \frac{2\mu}{\hbar^2}\underbrace{\langle (j'l')J0|\Delta V|(jl)J0\rangle}_{\text{simplify}}$$

Boundary conditions

$$|\psi^{(jlJM)}(R)\rangle \cong |(jl)JM\rangle\frac{v_{jl}(R)}{R} - \sum_{j'l'}|(j'l')JM\rangle\frac{u_{j'l'}(R)}{R}S^{J,*}_{j'l';jl}(E)$$

with

$$|\psi^{(jlJM)}(R)\rangle = \sum_{j'l'}|(j'l')JM\rangle\frac{1}{R}f^{(jlJM)}_{j'l'}(R)$$

where

$$f^{(jlJM)}_{j'l'}(R) \cong \overset{\text{out}}{v_{jl}}(R)\delta_{j'j}\delta_{l'l} - \overset{\text{in}}{u_{j'l'}}(R)S^{J,*}_{j'l';jl}(E)$$

$$|\hat{k}E^-jm_j\rangle = \sum_{JM}\left[\frac{k_j\mu}{\hbar(2\pi)^3}\right]^{1/2}4\pi\sum_{lm_l}\frac{i^l}{2i}|\psi^{(jlJM)}\rangle\left[\frac{\hbar}{\mu k_j}\right]^{1/2}Y^*_{lm_l}(\theta_k\phi_k)$$
$$\times\langle jm_j\,lm_l|JM\rangle$$

Verify outgoing part

$$\sum_{JM}|\psi^{(jlJM)}\rangle\langle jm_j\,lm_l|JM\rangle = \sum_{JMj'l'}|(j'l')JM\rangle\cdot\frac{1}{R}v_{jl}(R)\delta_{j'j}\delta_{l'l}$$
$$\langle jm_j\,lm_l|JM\rangle$$

$$= \sum_{JM}\sum_{m_j'm_l'}|j'm_j'l'm_l'\rangle\langle j'm_j'l'm_l'|JM\rangle\langle JM|jm_j\,lm_l\rangle\delta_{j'j}\delta_{l'l}\frac{v_{jl}(R)}{R}$$

$$= |jm_j\rangle|lm_l\rangle\frac{v_{jl}(R)}{R}$$

$$|\hat{k}E^-jm_j\rangle = \left[\frac{k_j\mu}{\hbar(2\pi)^3}\right]^{1/2}4\pi\sum_{lm_l}\frac{i^l}{2i}|jm_j\rangle|lm_l\rangle\underbrace{\frac{v_{jl}(R)}{R}\left[\frac{\hbar}{\mu k_j}\right]^{1/2}}_{i\,h_l^{(1)}(k_j\cdot R)}Y^*_{lm_l}(\theta_k\phi_k)$$

Simplify

$$|\hat{k}E^-jm_j\rangle = \frac{1}{\sqrt{2\pi}}\sum_{lm_l}i^{l-1}\sum_{JM}|\psi^{(jlJM)}(R)\rangle\langle JM|jm_j\,lm_l\rangle Y^*_{l,m_l}(\theta_k,\phi_k)$$

Photodissociation cross section, SF, coupled

$$\sigma(\hat{k} E j m_j | i) = \frac{4\pi^2\omega}{c} \left| \langle \hat{k} E j m_j | \hat{e}\cdot\mu | i \rangle \right|^2$$

$$\langle \hat{k} E j m_j | \hat{e}\cdot\mu | i \rangle = \frac{1}{\sqrt{2\pi}} \sum_{\substack{l m_l \\ J M}} i^{-l+1} \underbrace{\langle \psi^{(jl)JM} | \hat{e}\cdot\mu | i \rangle}_{M_{jlJM;i}} \langle j m_j\, l m_l | J M \rangle Y^*_{l m_l}(\theta_k \phi_k)$$

$$\sigma(\hat{k} E j m_j | i) = \frac{4\pi^2\omega}{c}\cdot\frac{1}{2\pi} \sum_{JJ'MM'll'm_l m_l'} i^{l-l'} Y^*_{l m_l}(\theta_k \phi_k) Y_{l' m_l'}(\theta_k \phi_k)$$

$$M^*_{jlJM;i}\, M_{jl'J'M';i}\, \langle j m_j\, l m_l | J M \rangle \langle j m_j\, l' m_l' | J' M' \rangle$$

$$\boxed{\int \to \delta_{ll'}\, \delta_{m_l m_l'}} \quad \boxed{M = m_j + m_l = m_j + m_l' = M'}$$

$$\sigma^{m_j}_{tot}(E j m_j | i) = \frac{2\pi\omega}{c} \sum_{JJ'M l m_l} M^*_{jlJM;i}\, M_{jlJ'M;i}\, \langle j m_j\, l m_l | J M \rangle \langle j m_j\, l m_l | J' M \rangle$$

$$\left[\sum_{m_j m_l} \to \delta_{JJ'}\, \delta_{MM'}\right]$$

$\sigma_{tot}(E j | i)$

$$\sigma_{tot} = \sum_{m_j} \sigma^{m_j}_{tot} = \frac{2\pi\omega}{c} \sum_{JMl} M^*_{jlJM;i}\, M_{jlJM;i}$$

$$= \frac{2\pi\omega}{c} \sum_{JMl} \left| M_{jlJM;i} \right|^2$$

Uncoupled basis $|jm\rangle_{SF}\; Y_{lm'}(\hat{R})$

coupled $\quad |(jl)JM\rangle = \sum_{mm'} |jm\rangle\, |lm'\rangle \langle jm\, lm' | JM\rangle$

BF $\quad |jm\rangle_{BF} = \hat{R}\, |jm\rangle_{SF}$

$$|jm\rangle_{SF} = \hat{R}^{-1} |jm\rangle_{BF} = \sum_{k} |jk\rangle_{BF} \langle jk | R^{-1} | jm\rangle = \sum_{k} |jk\rangle_{BF}\, D^{j,*}_{m,k}(\hat{R})$$

$$|(jl)JM\rangle = \sum_{mm'} |jm\rangle_{SF}\, Y_{lm'}(\hat{R}) \langle jm\, lm' | JM\rangle$$

$$= \sum_{mm'k} |jk\rangle_{BF}\, D^{j,*}_{m,k}(\hat{R})\, D^{l,*}_{m',0}(\hat{R}) \sqrt{\frac{2l+1}{4\pi}} \langle jm\, lm' | JM\rangle$$

$$D^{j,*}_{m,k}(\hat{R})\, D^{l,*}_{m',0} = \sum_{J'M'K'} \langle jm\, lm' | J'M'\rangle \langle jk\, l0 | JK'\rangle\, D^{J',*}_{M'K'}(\hat{R})$$

$$|(jl)JM\rangle = \sum_{mm'kJ'M'K'} |jk\rangle_{BF}\, D^{J',*}_{M'K'}(\hat{R}) \sqrt{\frac{2l+1}{4\pi}}$$

$$\langle jm\, lm' | J'M'\rangle \underbrace{\langle jk\, l0 | JK'\rangle}_{\to\, \delta_{kK'}} \langle jm\, lm' | JM\rangle$$

$$\sum_{mm'} \langle jm\, lm' | J'M'\rangle \langle jm\, lm' | JM\rangle = \delta_{JJ'}\, \delta_{MM'}$$

$$|(jl)JM\rangle = \sum_{k} |jk\rangle_{BF}\, D^{J,*}_{MK}(\hat{R}) \sqrt{\frac{2l+1}{4\pi}} \langle jk\, l0 | JK\rangle$$

$$= \sum_{K} |jK\rangle_{BF}\, D^{J,*}_{MK}(\hat{R}) \sqrt{\frac{2J+1}{4\pi}} \sqrt{\frac{2l+1}{2J+1}} \langle jK\, l0 | JK\rangle$$

$$|(jk)JM\rangle_{BF} \equiv |jK\rangle_{BF}\, D^{J,*}_{MK}(\hat{R}) \sqrt{\frac{2J+1}{4\pi}}$$

$$|(jl)JM\rangle_{SF} = \sum_{k} |(jk)JM\rangle_{BF}\, U^{J,j}_{k,l}$$

$$U^{J,j}_{k,l} = \sqrt{\frac{2l+1}{2J+1}} \langle jk\, l0 | Jk\rangle$$

$$|(jk)JM\rangle_{BF} = \sum_{l} U^{J,j}_{k,l}\, |(jl)JM\rangle_{SF}$$

$\hookrightarrow$ real, unitary $\Rightarrow$ orthogonal
orthonormal

Coupled, BF $\displaystyle = \sum_{l} |jlJM\rangle_{SF}\, u^{Jj}_{kl}$

$$|(jk)JM\rangle_{BF} = \sum_{l m_l m_j} |jm_j\rangle |lm_l\rangle \langle jm_j\, lm_l | JM\rangle\, u^{J,j}_{k,l}$$

$$|\Psi(R)\rangle = \sum_{jkJM} |kjkJM\rangle_{BF} \frac{1}{R} f_{jkJM}(R)$$

$(H-E)|\Psi\rangle = 0 \qquad H_0 |jkJM\rangle_{BF} = \varepsilon_j |jkJM\rangle_{BF} \qquad [\vec{R}, H_0] = 0$

$\underline{f}''(R) = W(R)\underline{f}$

$$W_{j'k'J'M';jkJM}(R) = \langle j'k'J'M'| \frac{\hat{l}^2}{\hbar^2 R^2} + \frac{2\mu}{\hbar^2 R^2}(H_0 - E) + \frac{2\mu}{\hbar^2}\Delta V(R;q)|jkJM\rangle$$

$$= W^J_{j'k';jk}(R)\, \delta_{J'J}\delta_{M'M}$$

$$\langle j'k'J'M'|\hat{l}^2|jkJM\rangle = \sum_l l(l+1)(2l+1)\begin{pmatrix} j' & l & J' \\ k' & 0 & -k' \end{pmatrix}\begin{pmatrix} j & l & J \\ k & 0 & -k \end{pmatrix}$$

$$= \delta_{j'j}\delta_{J'J}\delta_{M'M}\Big[\delta_{k'k}\big[J(J+1) + j(j+1) - 2k^2$$

$$- \delta_{k',k\pm 1} \{\,[J(J+1) - k(k\pm 1)]^{1/2}[j(j+1) - k(k\pm 1)]^{1/2}$$

$$\langle j'k'J'M'|\frac{2\mu}{\hbar^2 R^2}(H_0 - E)|jkJM\rangle = -k_j^2\, \delta_{JJ'}\delta_{M'M}\delta_{j'j}\delta_{k'k}$$

$$\langle j'k'J'M'|\frac{2\mu}{\hbar^2}\Delta V(R;q)|jkJM\rangle = \delta_{J'J}\delta_{M'M}\langle j'k'|\frac{2\mu}{\hbar}\Delta V(R;q_{BF})|jk\rangle$$

Boundary conditions BF

$$|\Psi^{jkJM}(R)\rangle = |jkJM\rangle \frac{\tilde{v}_{j\cancel{k}}(R)}{R} - \sum_{j'k'} |j'k'JM\rangle \frac{\tilde{u}_{j\cancel{k}}(R)}{R} S^{J,*}_{j'k';jk}(E)$$

with

$$|\Psi^{jkJM}(R)\rangle = \sum_{j'k'} |j'k'JM\rangle \frac{1}{R} f^{jkJ}_{j'k'}(R)$$

where

$$f^{jkJ}_{j'k'}(R) \cong \tilde{v}_{j\cancel{k}}(R)\delta_{j'j}\delta_{k'k} - \tilde{u}_{j\cancel{k}}(R)\, S^{J,*}_{j'k';jk}(E)$$

$$\tilde{v}_{j\cancel{k}}(R) \equiv e^{ik_j\cdot R}\left[\frac{\mu}{\hbar k_j}\right]^{1/2} \qquad \tilde{u}_{j\cancel{k}}(R) = \tilde{v}^*_{j\cancel{k}}(R)$$

$$e^{-il\frac{\pi}{2}} = i^{-l} \Rightarrow i^{-l}\tilde{v}_{j\cancel{k}} \sim i h^{(1)}_l(k_n\cdot R)\left[\frac{\mu k_j}{\hbar}\right]^{1/2}$$

~~[illegible]~~

$$i^{-l}\tilde{v}_j(R) \cong v_{jl}(R)$$

$$|\hat{k}\, E^- j m_j\rangle = \sum_{JM}\left[\frac{k_j \mu}{\hbar (2\pi)^3}\right]^{1/2} 4\pi \sum_{lk m_l} \frac{1}{2i}\, |\psi^{jkJM}(R)\rangle\, U^{J,j}_{k,l}\left[\frac{\hbar}{\mu k_j}\right]^{1/2} Y^*_{l m_l}(\theta_k, \phi_k)$$

$$\langle j m_j\, l m_l | J M\rangle$$

Verify outgoing part

$$\sum_{JMk} i^{-l}|\psi^{jkJM}(R)\rangle U^{J,j}_{k,l}\langle j m_j\, l m_l | JM\rangle$$

$$= \sum_{JMk} i^{-l}\, |j k J M\rangle U^{J,j}_{k,l}\frac{\tilde{v}_j(R)}{R}\langle j m_j\, l m_l | JM\rangle$$

$$= \sum_{JM} |j l J M\rangle \frac{i^{-l}\tilde{v}_j(R)}{R}\langle j m_j\, l m_l | JM\rangle$$

$\rightarrow$ as in coupled SF using $i^{-l}\tilde{v}_j(R) \sim v_j(R)$

Compare SF/BF.

SF

$$|\hat{k}\, E^- j m_j\rangle = \sum_{JM}\left[\frac{k_j \mu}{\hbar (2\pi)^3}\right]^{1/2} 4\pi \sum_{l m_l}\frac{i^l}{2i}\, |\psi^{jlJM}\rangle_{SF}\left[\frac{\hbar}{\mu k_j}\right]^{1/2} Y^*_{l m_l}(\theta_k, \phi_k)$$

$$\times \langle j m_j\, l m_l | JM\rangle$$

BF

$$|\hat{k}\, E^- j m_j\rangle = \sum_{JM}\left[\frac{k_j \mu}{\hbar (2\pi)^3}\right]^{1/2} 4\pi \sum_{l m_l}\sum_{k}\frac{1}{2i}\, |\psi^{jkJM}(R)\rangle\, U^{Jj}_{kl}\left[\frac{\hbar}{\mu k_j}\right]^{1/2} Y^*_{l m_l}(\theta_k, \phi_k)$$

$$\langle j m_j\, l m_l | JM\rangle$$

Thus

$$i^l|\psi^{jlJM}(R)\rangle = \sum_k |\psi^{jkJM}(R)\rangle U^{Jj}_{k,l}$$

$$i^l|\psi^{jlJM}(R)\rangle = |j l J M\rangle \frac{i^l v_{jl}(R)}{R} - \sum_{j'l'} |j' l' J M\rangle \frac{i^l u_{j'l'}(R)}{R} S^{J,*}_{j'l';jl}$$

$$\sum_k |\psi^{jkJM}(R)\rangle U^{Jj}_{k,l}(R) = \sum_k |j k J M\rangle U^{Jj}_{kl}\frac{\tilde{v}_j(R)}{R} + \sum_{j'l'} |j' l' J M\rangle \frac{\tilde{u}_{j'}}{R} S^{J,*}_{j'l';jl} \times U^{Jj}_{kl}$$

Check incoming part (again)

$$\sum_k |jkJM\rangle\, u^{Jj}_{kl}(\cancel{R}) = |(jl)JM\rangle \; ; \; i^l v_{jl}(R) \overset{?}{=} \tilde{v}_j(R)$$

OK

outgoing parts:

$$\sum_{j'l'} |(j'l')JM\rangle \frac{i^l u_{j'l'}(R)}{R} S^{J,*}_{j'l';jl}$$

$$= \sum_{j'k'k} |j'k'JM\rangle \frac{\tilde{u}_{j'}(R)}{R} S^{J,*}_{j'k';jk}\, U^{Jj}_{kl}$$

$$= \sum_{j'k'kl'} |(j'l')JM\rangle\, U^{Jj'}_{l'k'} \frac{\tilde{u}_{j'}(R)}{R} S^{J,*}_{j'k';jk}\, U^{Jj}_{kl}$$

Asymptotic: $\left[\frac{\mu}{\hbar k_j}\right]^{1/2} \times$

$$i^l u_{j'l'}(R) \sim e^{-ik_jR} \left(e^{i\frac{\pi}{2}}\right)^{l'} i^l \cancel{=} = e^{-ik_jR}\, i^{l'+l}$$

$$\tilde{u}_{j'}(R) \sim e^{-ik_{j'}R} \;\cancel{\sim e^{-l'-l}\, i^l u_{j'l'}(R)}$$

$$\cancel{= i^{-l'} u_{j'l'}(R)}$$

$$= \sum_{j'l'} |(j'l')JM\rangle \sum_{kk'} \frac{e^{-ik_jR}}{R} U^{Jj'}_{l'k'} S^{J,*}_{j'k';jk}\, U^{Jj}_{kl}$$

$$= \sum_{j'l'} |(j'l')JM\rangle\, i^{l'+l} \frac{e^{-ik_jR}}{R} S^{J,*}_{j'l';jl}$$

$$\cancel{\varepsilon} \quad i^{l'+l} S^{J,*}_{j'l';jl} = U^{Jj'}_{l'k'} S^{J,*}_{j'k';jk}\, U^{Jj}_{kl}$$

$$S^{J}_{j'l';jl} = i^{l'+l}\, U^{Jj'}_{l'k'} S^{J}_{j'k';jk}\, U^{Jj}_{kl}$$

Simplify

$$|k E^- j m_j\rangle = \frac{i}{\sqrt{2\pi}} \sum_{l m_l J M k} |\psi^{jkJM}(R)\rangle\, U^{J,j}_{k,l} \langle JM | j m_j l m_l\rangle\, Y^*_{l m_l}(\theta_k, \phi_k)$$

Photodissociation cross section BP

$$\sigma(\hat{k} E^- j m_j | i) = \frac{4\pi^2\omega}{c} \left| \langle \hat{k} E^- j m_j | \hat{e}\cdot\mu | i\rangle \right|^2$$

$$\langle \hat{k} E^- j m_j | \hat{e}\cdot\mu | i\rangle = \frac{i}{\sqrt{2\pi}} \sum_{l m_l J M k} \underbrace{\langle \psi^{jkJM}(R) | \hat{e}\cdot\mu | i\rangle}_{M_{jkJM;i}} U^{J,j}_{kl} \langle JM | j m_j l m_l\rangle\, Y_{l m_l}(\theta_k, \phi_k)$$

$$\sigma(\hat{k} E^- j m_j | \cancel{\hat{e}\cdot\mu} | i) = \frac{2\pi\omega}{c} \sum_{l l' m_l m_l' J J' M M' k k'} Y^*_{l m_l}(\theta_k \phi_k)\, Y_{l' m_l'}(\theta_k, \phi_k)$$

$$M^*_{jkJM;i}\, M_{jk'J'M';i}\, U^{Jj}_{kl}\, U^{J'j}_{k'l'}$$

$$\langle JM | j m_j l m_l\rangle \langle J'M' | j m_j l' m_l'\rangle$$

$$\iint d\cos\theta_k\, d\phi_k \rightarrow \delta_{ll'}\delta_{m_l m_l'}$$

$$\sigma(\cancel{\hat{k}} E^- j m_j | i) = \frac{2\pi\omega}{c} \cancel{\sum_{l m_l}} \sum_{k k' J J' M M'} M^*_{jkJM;i}\, M_{jk'J'M'}$$

$$\sum_{l m_l} U^{Jj}_{kl}\, U^{J'j}_{k'l} \langle JM | j m_j l m_l\rangle \langle J'M' | j m_j l m_l\rangle$$

$\underline{\sum m_j}$ $\quad \sum_{m_j m_l} \rightarrow \delta_{JJ'}\delta_{MM'}$

$$\sigma(E^- j | i) = \frac{2\pi\omega}{c} \sum_{k k' J M} M^*_{jkJM;i}\, M_{jk'JM} \sum_l \underbrace{U^{Jj}_{kl}\, U^{Jj}_{k'l}}_{\delta_{kk'}}$$

$$= \frac{2\pi\omega}{c} \sum_{JMk} |M_{jkJM}|^2$$