水素分子の VB 法に現れる J と K

原子軌道：$\phi_a(1)=\phi_a(r_{a1})=(1/\sqrt{\pi})\exp(-r_{a1})$,　$\phi_b(2)=\phi_b(r_{b2})=(1/\sqrt{\pi})\exp(-r_{b2})$
（原子単位系をとったことに相当）
積分の定義：

$$S\equiv\int dv_1\phi_a{}^*(1)\phi_b(1)$$

$$J\equiv\int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)\left(-\frac{1}{r_{b1}}-\frac{1}{r_{a2}}-+\frac{1}{r_{12}}+\frac{1}{R}\right)\phi_a(1)\phi_b(2)$$

$$K\equiv\int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)\left(-\frac{1}{r_{b1}}-\frac{1}{r_{a2}}-+\frac{1}{r_{12}}+\frac{1}{R}\right)\phi_a(1)\phi_b(2)$$

積分の具体的な形：

$$S=\int dv_1\phi_a{}^*(1)\phi_b(1)=e^{-R}\left(1+R+R^3/3\right)$$

$$J=-\left(b|aa\right)-\left(a|bb\right)-\left(aa|bb\right)+1/R$$

$$K=-S\left(b|ab\right)-S\left(a|ab\right)+\left(ab|ab\right)+S^2/R$$

但し，

$$\left(a|bb\right)=\left(b|aa\right)=\int dv_1\frac{\phi_a(1)\phi_a(1)}{r_{b1}}=\frac{1}{R}\left\{1-e^{-2R}(1+R)\right\}$$

$$\left(a|ab\right)=\left(b|ab\right)=\int dv_1\frac{\phi_a(1)\phi_b(1)}{r_{b1}}=e^{-R}(1+R)$$

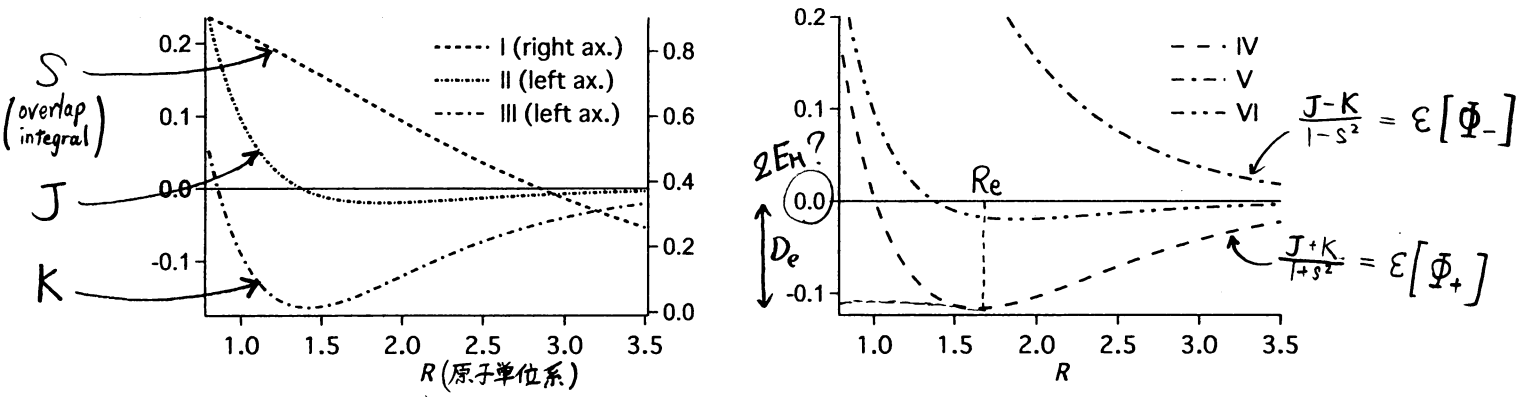
$$\left(aa|bb\right)=\int dv_1\,dv_2\phi_a(1)\phi_a(1)\frac{1}{r_{12}}\phi_b(2)\phi_b(2)=\frac{1}{R}\left\{1-\left(1+\frac{11}{8}R+\frac{3}{4}R^2+\frac{1}{6}R^3\right)e^{-2R}\right\}$$

$$\left(ab|ab\right)=\int dv_1\,dv_2\phi_a(1)\phi_b(1)\frac{1}{r_{12}}\phi_1(1)\phi_b(2)=\frac{1}{5}\left[\begin{array}{l}-e^{-2R}\left(-\frac{25}{8}+\frac{23}{4}R+3R^2+\frac{1}{3}R^3\right)\\+\frac{6}{R}\left\{S^2(\gamma+\ln R)-2S\Delta\,E_i(-2R)+\Delta^2\,E_i(-4R)\right\}\end{array}\right]$$

$$\Delta=e^R\left(1-R+R^3/3\right)$$

$\gamma=0.5772156649\ldots$: Euler's constant

$E_i(-r)=\int_r^\infty\frac{e^{-x}}{x}dx$: exponential integral, ex) $E_i(-1)=0.219384$



I: S, II: J, III: K, IV: $\frac{J+K}{1+S^2}$, V: $\frac{J-K}{1-S^2}$, VI: J →

ひきはなすと H原子 2つになるような挙動

（参考）　長倉・中島編，化学と量子論，1979、岩波書店.

長さの場合は、$a_0=\frac{\hbar^2}{me^2}=5.29\ldots\times10^{-11}$ [m]
$(\fallingdotseq 0.5\,\text{Å})$

水素分子の VB 波動関数の Rayleigh 比

ハミルトニアン

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R}\right)$$

$$= -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{a1}} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{b2}} + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}} + \frac{1}{R}\right)$$

$$= H_a(1) + H_b(2) + V(1,2) = H_a(2) + H_b(1) + V(2,1),$$

$$H_a(1) \equiv -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{a1}},\quad H_b(2) \equiv -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{b2}},\quad V(1,2) \equiv \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}} + \frac{1}{R}\right)$$

$$H_a(2) \equiv -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{a2}},\quad H_b(1) \equiv -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{b1}},\quad V(2,1) \equiv \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{b2}} - \frac{1}{r_{a1}} + \frac{1}{r_{12}} + \frac{1}{R}\right)$$

波動関数　$\Phi_\pm = \phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)$

積分の定義

$J \equiv \int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)V\phi_a(1)\phi_b(2)$:Coulombic integral

$K \equiv \int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)V\phi_a(1)\phi_b(2)$:Exchange integral

$S \equiv \int dv_1\phi_a{}^*(1)\phi_b(1)$:Overlap integral

(1) $\int dv_1\,dv_2\Phi_\pm{}^*(1,2)\Phi_\pm(1,2) = 2(1 \pm S^2)$

∵)

$$\int dv_1\,dv_2\Phi_\pm{}^*(1,2)\Phi_\pm(1,2)$$

$$= \int dv_1\,dv_2\{\phi_a{}^*(1)\phi_b{}^*(2) \pm \phi_b{}^*(1)\phi_a{}^*(2)\}\{\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)\}$$

$$= \int dv_1\phi_a{}^*(1)\phi_a(1)\int dv_2\phi_b{}^*(2)\phi_b(2) \pm \int dv_1\phi_a{}^*(1)\phi_b(1)\int dv_2\phi_b{}^*(2)\phi_a(2)$$

$$\pm\int dv_1\phi_b{}^*(1)\phi_a(1)\int dv_2\phi_a{}^*(2)\phi_b(2) + \int dv_1\phi_b{}^*(1)\phi_b(1)\int dv_2\phi_a{}^*(2)\phi_a(2)$$

$$= 1 \pm S^2 \pm S^2 + 1 = 2(1 \pm S^2)$$

(2) $\int dv_1\,dv_2\Phi_\pm{}^*(1,2)H\Phi_\pm(1,2) = 2(2E_H(1 \pm S^2) + J \pm K)$

∵)

$$\int dv_1\,dv_2\Phi_\pm{}^*(1,2)H\Phi_\pm(1,2)$$

$$= \int dv_1\,dv_2\{\phi_a{}^*(1)\phi_b{}^*(2) \pm \phi_b{}^*(1)\phi_a{}^*(2)\}H\{\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2)\}$$

$$= \int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)H\phi_a(1)\phi_b(2) \pm \int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)H\phi_b(1)\phi_a(2)$$

$$\pm\int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)H\phi_a(1)\phi_b(2) + \int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)H\phi_b(1)\phi_a(2)$$

ここで以下のように第１項＝第４項，第２項＝第３項なので，

$$\left[\begin{aligned}
\int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)H\phi_a(1)\phi_b(2) &= \int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)\{H_a(1)+H_b(2)+V(1,2)\}\phi_a(1)\phi_b(2)\\
&= \int dv_1\,dv_2\phi_a{}^*(2)\phi_b{}^*(1)\{H_a(2)+H_b(1)+V(2,1)\}\phi_a(2)\phi_b(1)\\
&= \int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)H\phi_b(1)\phi_a(2)\\
\int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)H\phi_b(1)\phi_a(2) &= \int dv_1\,dv_2\phi_a{}^*(1)\phi_b{}^*(2)\{H_a(1)+H_b(2)+V(1,2)\}\phi_b(1)\phi_a(2)\\
&= \int dv_1\,dv_2\phi_a{}^*(2)\phi_b{}^*(1)\{H_a(2)+H_b(1)+V(2,1)\}\phi_b(2)\phi_a(1)\\
&= \int dv_1\,dv_2\phi_b{}^*(1)\phi_a{}^*(2)H\phi_a(1)\phi_b(2)
\end{aligned}\right]$$

$$\int dv_1\, dv_2 \Phi_\pm^*(1,2) H \Phi_\pm(1,2)$$
$$= 2\left[\int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H \phi_a(1)\phi_b(2) \pm \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H \phi_b(1)\phi_a(2)\right]$$

第 1 項は次のようになる：

$$\int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H \phi_a(1)\phi_b(2) = \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2)\{H_a(1) + H_b(2) + V(1,2)\}\phi_a(1)\phi_b(2)$$
$$= \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H_a(1)\phi_a(1)\phi_b(2) + \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H_b(2)\phi_a(1)\phi_b(2)$$
$$+ \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) V(1,2)\phi_a(1)\phi_b(2)$$
$$= E_H + E_H + J = 2E_H + J$$

第 2 項は次のようになる：

$$\int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H \phi_b(1)\phi_a(2) = \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2)\{H_a(2) + H_b(1) + V(2,1)\}\phi_b(1)\phi_a(2)$$
$$= \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H_a(2)\phi_b(1)\phi_a(2) + \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) H_b(1)\phi_b(1)\phi_a(2)$$
$$+ \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) V(2,1)\phi_b(1)\phi_a(2)$$
$$= \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) E_H \phi_b(1)\phi_a(2) + \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) E_H \phi_b(1)\phi_a(2)$$
$$+ \int dv_1\, dv_2 \phi_a^*(1)\phi_b^*(2) V(2,1)\phi_b(1)\phi_a(2)$$
$$= E_H S^2 + E_H S^2 + K = 2E_H S^2 + K$$

以上より，

$$\int dv_1\, dv_2 \Phi_\pm^*(1,2) H \Phi_\pm(1,2) = 2(2E_H + J \pm (2E_H S^2 + K)) = 2(2E_H(1 \pm S^2) + J \pm K)$$

(3) Rayleigh 比

$$\varepsilon[\Phi_\pm] = \frac{\int dv_1\, dv_2 \Phi_\pm^*(1,2) H \Phi_\pm(1,2)}{\int dv_1\, dv_2 \Phi_\pm^*(1,2) \Phi_\pm(1,2)} = \frac{2(2E_H(1 \pm S^2) + J \pm K)}{2(1 \pm S^2)} = 2E_H + \frac{J \pm K}{1 \pm S^2}$$