

## Linear Variational Approximation

Let us do the variational method using a linear combination of the wave functions in the form:

$$|\phi\rangle = \sum_{n=1}^N c_n |f_n\rangle \quad (7-48)$$

Where the  $c_n$  are the variational parameters and  $|f_n\rangle$  the are arbitrary known functions. For simplicity we will assume  $N = 2$ ,  $c_n$  and  $|f_n\rangle$  are real.

Consider

$$\phi = c_1 f_1 + c_2 f_2$$

Then

$$\begin{aligned} \int \phi \hat{H} \phi d\tau &= \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) d\tau \\ &= c_1^2 \int f_1 \hat{H} f_1 d\tau + c_1 c_2 \int f_1 \hat{H} f_2 d\tau + c_1 c_2 \int f_2 \hat{H} f_1 d\tau + c_2^2 \int f_2 \hat{H} f_2 d\tau \\ &= c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22} \end{aligned} \quad (7-49)$$

where

$$H_{ij} = \int f_i \hat{H} f_j d\tau \quad (7-50)$$

Because  $\hat{H}$  is Hermitian,  $H_{ij} = H_{ji}$ , and so Eq. 7-49 becomes

$$\int \phi \hat{H} \phi d\tau = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22} \quad (7-51)$$

Similarly, we have

$$\int \phi^2 d\tau = c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22} \quad (7-52)$$

where

$$S_{ij} = S_{ji} = \int \phi_i \phi_j d\tau \quad (7-53)$$

The quantities  $H_{ij}$  and  $S_{ij}$  are called *matrix elements*. By substituting Eqs. 7-51 and 7-52 into Eq. 7-29, we find

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}} \quad (7-54)$$

where we emphasize here that  $E$  is a function of the variational parameters  $c_1$  and  $c_2$ .

Before differentiating  $E(c_1, c_2)$  in Eq. 7-54 with respect to  $c_1$  and  $c_2$ , it is convenient to write Eq. 7-54 in the form

$$E(c_1, c_2)(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22} \quad (7-55)$$

If we differentiate Eq. 7-55 with respect to  $c_1$ , we find

$$(2c_1 S_{11} + 2c_2 S_{12})E + \frac{\partial E}{\partial c_1} (c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12} \quad (7-56)$$

Because we are minimizing  $E$ ,  $\partial E/\partial c_1 = 0$  and so Eq. 7-56 becomes

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \quad (7-57)$$

Similarly, by differentiating  $E(c_1, c_2)$  with respect to  $c_2$  instead of  $c_1$ , we find that

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0 \quad (7-58)$$

Equations 7-57 and 7-58 constitute a pair of linear algebraic equations for  $c_1$  and  $c_2$ . According to the theory of linear algebraic equations, there is a nontrivial solution, that is, a solution that is not simply  $c_1 = c_2 = 0$ , if and only if the determinant of the coefficients vanishes or if and only if

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (7-59)$$

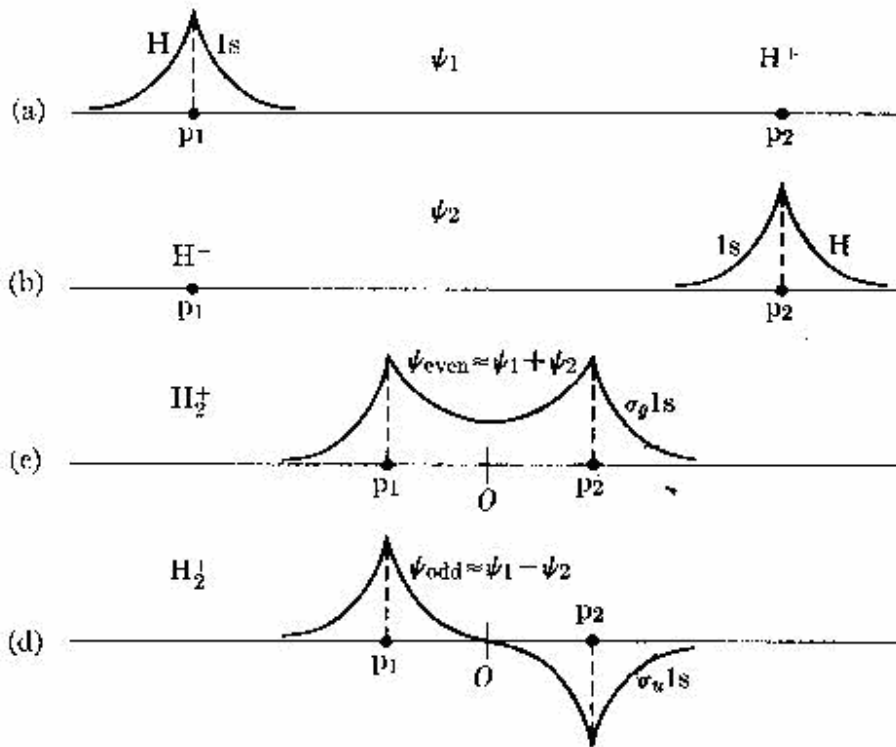
This determinant is called a *secular determinant*. When this  $2 \times 2$  determinant is expanded, we obtain a quadratic equation in  $E$ , called the *secular equation*. The quadratic secular equation gives two values for  $E$ , and we take the smaller of the two solutions as our approximation for the ground-state energy.

If we use a linear combination of  $N$  functions instead of using a linear combination of two functions as we have done so far, we obtain an  $N \times N$  secular determinant instead of a  $2 \times 2$  secular determinant:

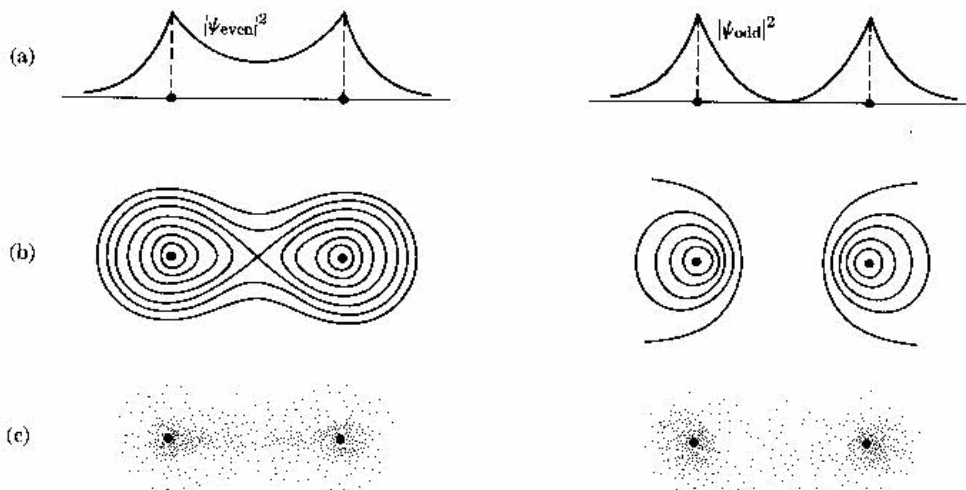
$$\begin{vmatrix} H_{11} - ES_{11} & H_{21} - ES_{21} & \cdots & H_{N1} - ES_{N1} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{N2} - ES_{N2} \\ \vdots & \vdots & & \vdots \\ H_{1N} - ES_{1N} & H_{2N} - ES_{2N} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (7-61)$$

The secular equation associated with this secular determinant is an  $N$ th-order polynomial in  $E$ . We choose the smallest root of the  $N$ th-order secular equation as an approximation to the energy. The determination of the smallest root must usually be done graphically or numerically for values of  $N$  larger than two. This is actually a standard numerical problem and there are a number of packaged computer routines that do this.

### Hydrogen molecule ion ( $H_2^+$ )

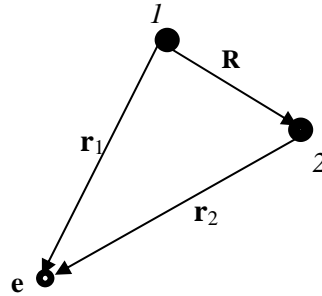


**Fig. 5-4.** Even and odd molecular orbitals in  $H_2^+$ .



**Fig. 5-5.** Probability density for even and odd molecular orbitals in  $H_2^+$ . (a) Distribution along the lines joining the protons; (b) and (c) distribution in a plane containing the two protons.

**Example:** For the Hydrogen molecule ion ( $H_2^+$ ), see the figure:



A coordinate system for the Hydrogen molecule ion ( $H_2^+$ )

work out the lowest energy states of the Hydrogen molecule ion ( $H_2^+$ ). Use the trial linear combination function in the form:

$$\varphi = a_1\psi_1 + a_2\psi_2; \quad (1)$$

Where

$$\psi_i = \frac{1}{\sqrt{\pi}} e^{-r_i}$$

And neglect the motion of the nucleus. Write your comments in the states.

[Hint: Write the electronic Hamiltonian  $\hat{H}$ , solve the secular determinant using the abbreviations  $H_{ij}, S_{ij}$ , where  $i$  and  $j$  take the values 1 and 2. and then calculate the integrals using the elliptical coordinate system.

**Answer:**

The Hamiltonian is given by (neglect the K.E. operator for the protons):

$$\hat{H} = -\frac{1}{2} \nabla_e^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R} \quad (2)$$

Define the integrals:

$$H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle = H_{ji};$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle = S_{ji}$$

Then the secular determinant will be:

$$\begin{vmatrix} (H_{11} - E) & (H_{12} - ES) \\ (H_{21} - ES) & (H_{22} - E) \end{vmatrix} = 0 \quad (3)$$

which we used the standards integrals and:

$$H_{11} = \langle \psi_1 | \hat{H} | \psi_1 \rangle = H_{22};$$

$$H_{12} = \langle \psi_1 | \hat{H} | \psi_2 \rangle = H_{21};$$

$$S_{11} = \langle \psi_1 | \psi_1 \rangle = S_{22} = 1;$$

$$S_{12} = \langle \psi_1 | \psi_2 \rangle = S_{21} = S$$

From (3), one finds:

$$H_{11} - E = \pm(H_{12} - E S) \quad (4)$$

And we get the roots of the lowest energy states:

$$E_+ = \frac{H_{11} + H_{12}}{1 + S} \quad (5)$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S}$$

To calculate the eigen functions, we use the equation:

$$a_1(H_{11} - E) + a_2(H_{12} - E S) = 0 \quad (6)$$

that gives (for the root  $E_+$ )  $a_2 = a_1$  and:

$$\varphi_+ = a_1(\psi_1 + \psi_2)$$

And for the root  $E_-$ , we have  $a_2 = -a_1$  and:

$$\varphi_- = a_1(\psi_1 - \psi_2)$$

### H.W.

a- Use  $\langle \varphi_+ | \varphi_+ \rangle = 1$  to proof  $a_1 = \frac{1}{\sqrt{2+2S}}$

b- Use  $\langle \varphi_- | \varphi_- \rangle = 1$  to proof  $a_1 = \frac{1}{\sqrt{2-2S}}$

Summary:

$$E_+ = \frac{H_{11} + H_{12}}{1 + S}, \quad \varphi_+ = \frac{\psi_1 + \psi_2}{\sqrt{2 + 2S}} \quad (\text{bonding orbital})$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S}, \quad \varphi_- = \frac{\psi_1 - \psi_2}{\sqrt{2 - 2S}} \quad (\text{antibonding orbital})$$

### Mathematical preliminarily

Use the H-wave equation:

$$\left( -\frac{1}{2} \nabla_i^2 - \frac{1}{r_i} \right) \psi_i(r) = -\frac{1}{2} \psi_i(r), \quad i = 1, 2$$

Then

$$H_{11} = -\frac{1}{2} + J$$

Where  $J$  is the Coulomb integral:

$$J = \langle \psi_1 | -\frac{1}{r_2} + \frac{1}{R} | \psi_1 \rangle$$

And

$$H_{12} = -\frac{S}{2} + K$$

Where  $K$  is the exchange integral:

$$K = \langle \psi_1 | -\frac{1}{r_1} + \frac{1}{R} | \psi_2 \rangle$$

Then

$$E_{\pm} = \frac{H_{11} \pm H_{12}}{1 \pm S} = -\frac{1}{2} + \frac{J \pm K}{1 \pm S};$$

$$\Delta E_{\pm} = E_{+} - E_{-} = \frac{J \pm K}{1 \pm S}$$

**H.W.** Use the Elliptic coordinate system to prove the following integrals:

$$S = (1 + R + \frac{R^2}{3})e^{-R}; \quad J = (1 + \frac{1}{R})e^{-2R}; \quad K = \frac{S}{R} - (1 + R)e^{-R}$$

**H.W.** Plot and discuss the following figure:

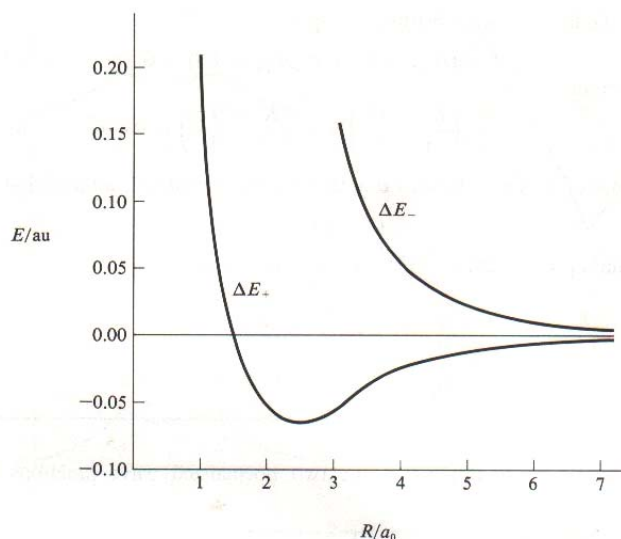


Figure 9-6. The energy as a function of internuclear separation for the  $H_2^+$  molecular ion

that are presented in Figure 9-6. The energy  $\Delta E_+$  describes a stable molecular species whose dissociation energy is  $0.065 \text{ au} = 1.77 \text{ eV}$  and whose equilibrium bond length is  $2.49 \text{ au} = 0.132 \text{ nm}$ , compared to the experimental values of  $0.102 \text{ au} = 2.78 \text{ eV}$  and  $2.00 \text{ au} = 0.106 \text{ nm}$ , respectively. If we simply use  $1s$  orbitals with the exponent as a variational parameter, then we obtain a dissociation energy of  $0.083 \text{ au} = 2.25 \text{ eV}$  and a bond length of  $2.00 \text{ au} = 0.106 \text{ nm}$ .

Although we could obtain increasingly better values of the energy and bond length of  $H_2^+$ , we are primarily interested in the corresponding wave functions.

## Types of Molecular Orbitals

### Bonding Orbitals

For the linear combination of only two atomic orbitals, the bonding orbital is constructed from adding the wavefunctions together.

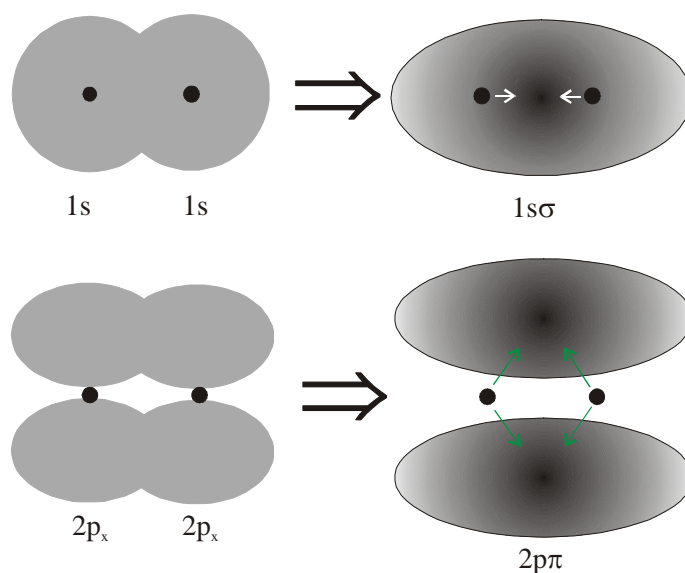
$$\Psi_{MO} = \Psi_{AO}(A) + \Psi_{AO}(B)$$

Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\Psi_{MO}|^2 &= |\Psi_{AO}(A)|^2 + |\Psi_{AO}(B)|^2 + 2\Psi_{AO}(A)\Psi_{AO}(B) \\ &= A^2 + B^2 + 2AB \end{aligned}$$

The  $2AB$  term is the constructive interference of the overlap of the atomic orbitals.

- The interference results in an increase of electron density between the nuclei.
- Thus, the nuclei have greater attraction to each other, via their mutual attraction to the increased electron density.



Aside:  $S = \int AB d\tau$  is called **overlap integral**.

### Antibonding Orbitals

For the linear combination of only two atomic orbitals, the antibonding orbital is constructed from subtracting the wavefunctions together.

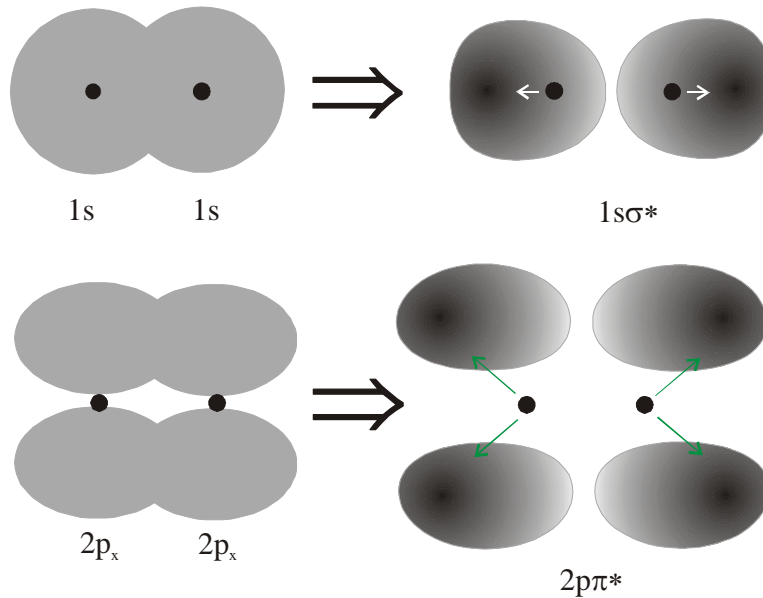
$$\Psi_{MO} = \Psi_{AO}(A) - \Psi_{AO}(B)$$

Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\Psi_{MO}|^2 &= |\Psi_{AO}(A)|^2 + |\Psi_{AO}(B)|^2 - 2\Psi_{AO}(A)\Psi_{AO}(B) \\ &= A^2 + B^2 - 2AB \end{aligned}$$

The  $-2AB$  term is the destructive interference of the overlap of the atomic orbitals.

- The interference results in a decrease of electron density between the nuclei and increase of electron density away from the nuclei.
- Thus, the nuclei are drawn away from each other.



The energy increase of the antibonding orbital is slightly higher than the energy decrease of the bonding orbital.

$$E_{\pm} \propto \frac{1}{1 \pm S} \quad (S \text{ is the overlap integral})$$

Example: Let  $S = \frac{1}{4}$

$$E_{+} \propto \frac{1}{1+S} = \frac{1}{1+\frac{1}{4}} = \frac{1}{\frac{5}{4}} = \frac{4}{5}$$

$$E_{-} \propto \frac{1}{1-S} = \frac{1}{1-\frac{1}{4}} = \frac{1}{\frac{3}{4}} = \frac{4}{3}$$

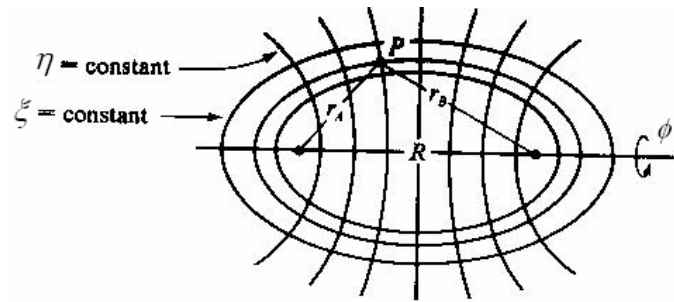


## Evaluation of two-center integrals

The overlap integral and other integrals that arise in two-center problems like  $H_2$ , such as:

$$\mathfrak{S} = \int \frac{e^{-pr_A} e^{-qr_B}}{r_A r_B} d\tau, \quad d\tau = d\tau_A d\tau_B \quad [A9.1]$$

are called two-center integrals. Two-center integrals are most easily evaluated by using a coordinate system called **confocal elliptic** coordinates.



Elliptic coordinates.

In this coordinate system (See Figure), there are two fixed points, separated by a distance  $R$ . A point  $P$  is given by the three coordinates:

$$\xi = \frac{(r_A + r_B)}{R}, \quad 1 \leq \xi \leq \infty \quad [A9.2]$$

$$\eta = \frac{(r_A - r_B)}{R}, \quad -1 \leq \eta \leq +1$$

and the azimuthal angle  $\phi$   $0 \leq \phi \leq 2\pi$ , which is the angle that the  $(r_A, r_B, R)$  triangle makes about the interfocal axis (take it z-axis). Note:  $r_A = \frac{R}{2}(\xi + \eta)$  and  $r_B = \frac{R}{2}(\xi - \eta)$ ,

$\xi^2 - \eta^2 = \frac{4r_A r_B}{R^2}$ . The volume integral is given by:

$$d\tau_A d\tau_B = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi \quad [A9.3]$$

So that:

$$\mathfrak{J} = \frac{R}{2} \int_1^\infty d\xi \int_{-1}^{+1} d\eta \int_0^{2\pi} d\phi e^{-a\xi - b\eta} \quad [A9.4]$$

where

$$a = \frac{R}{2} (p + q) \quad [A9.5]$$

$$b = \frac{R}{2} (p - q)$$

The integral [A9.4] is now elementary and is given by

$$\begin{aligned} \mathcal{J} &= \frac{\pi R}{ab} e^{-a}(e^b - e^{-b}) \\ &= \frac{4\pi}{R} \frac{1}{p^2 - q^2} (e^{-qR} - e^{-pR}) \end{aligned} \quad [\text{A9.6}]$$

The other relevant integrals are obtained by differentiating the above result with respect to  $p$  and  $q$ . That is,

$$\begin{aligned} K &= \int \frac{e^{-pr_A} e^{-qr_B}}{r_A} dr = - \frac{\partial}{\partial q} \mathcal{J} \\ &= \frac{4\pi}{R} \left[ \frac{R}{p^2 - q^2} e^{-qR} + \frac{2q}{(p^2 - q^2)^2} (e^{-pR} - e^{-qR}) \right] \end{aligned} \quad [\text{A9.7}]$$

and

$$\begin{aligned} L &= \int e^{-pr_A} e^{-qr_B} dr = - \frac{\partial}{\partial p} K \\ &= \frac{8\pi}{R(p^2 - q^2)^2} \left[ R(pe^{-qR} + qe^{-pR}) + \frac{4pq}{p^2 - q^2} (e^{-pR} - e^{-qR}) \right] \end{aligned} \quad [\text{A9.8}]$$

In the particular case  $p = q$ , we have

$$\mathcal{J} = \frac{2\pi}{p} e^{-pR} \quad [\text{A9.9}]$$

$$K = \frac{\pi}{p^2} (1 + pR) e^{-pR} \quad [\text{A9.10}]$$

and

$$L = \frac{\pi}{p^3} \left( 1 + pR + \frac{1}{3} p^2 R^2 \right) e^{-pR} \quad [\text{A9.11}]$$

## Elliptic coordinates

Calculate the integral  $I = \int |\psi(r_1, r_2)|^2 \frac{1}{r_{12}} d\tau_1 d\tau_2$ , where  $\psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$  using the elliptic coordinate.

The elliptic coordinates is defined by the variables:

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12};$$

$$-u \leq t \leq u, \quad 0 \leq u \leq s \leq \infty;$$

$$d\tau_1 d\tau_2 = \pi^2 (s^2 - t^2) u ds dt du$$

Then for the wave function:  $\psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$ , we can have:

$$\begin{aligned} I &= \int |\psi(r_1, r_2)|^2 \frac{1}{r_{12}} d\tau_1 d\tau_2 = \pi^2 \left( \frac{Z^3}{\pi} \right)^2 \int_0^\infty ds \int_0^s du \int_{-u}^u e^{-2Zs} \left( \frac{s^2 - t^2}{u} \right) dt \\ &= \frac{5}{8} Z \end{aligned}$$