

1. Many of the equations used in quantum chemistry can be usefully simplified by transforming to **atomic units** (au) given to us by nature. For example, instead of using meters for the unit of length, we use the Bohr radius a_0 as the “natural” unit of length. Instead of using the kilogram for the unit of mass, we use the electron mass, and so on.

Quantity	Atomic Unit	Equivalent SI Value
mass	$m = 1$ (electron mass)	9.1091×10^{-31} kg
charge	$ e = 1$ (proton charge)	1.6021×10^{-19} C
angular momentum	$\hbar = 1$	1.0545×10^{-34} J s
vacuum permittivity	$\kappa_0 = 4\pi\epsilon_0 = 1$	1.1126×10^{-10} C ² J ⁻¹ m ⁻¹
length	$a_0 = \kappa_0 \hbar^2 / m e^2 = 1$ (Bohr radius)	5.2917×10^{-11} m
energy	$m e^4 / \kappa_0^2 \hbar^2 = e^2 / \kappa_0 a_0 = 1$ (Hartree = $2 E_{1s} $)	4.3594×10^{-18} J
time	$\kappa_0^2 \hbar^3 / m e^4 = 1$ (travel time for 1s Bohr orbit)	2.4189×10^{-17} s
speed	$e^2 / \kappa_0 \hbar = 1$ (electron speed in 1s Bohr orbit)	2.1876×10^8 m s ⁻¹
magnetic dipole moment	$e \hbar / m = 1$ (two Bohr magnetons)	1.8546×10^{-23} J T ⁻¹
electric potential	$m e^3 / \kappa_0^2 \hbar^2 = e / \kappa_0 a_0 = 1$ (in 1s Bohr orbit)	27.211 V

- a) Show that the ground state energy of the He⁺ ion is -2 au = -2 Hartrees.
- b) Show that the speed of light is equal to 137.0 au.
- c) Show that the equation for the wave equation for the 1s orbital of a hydrogen-like atom

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

transformed to atomic units is

$$\psi_{1s} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

- d) In class, we derived the expression

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla_{e1}^2 - \frac{\hbar^2}{2m_e} \nabla_{e2}^2 - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$

for the Hamiltonian for the H₂ molecule. In atomic units, show that the equation simplifies considerably to

$$\hat{H}_e = -\frac{1}{2}(\nabla_{e1}^2 + \nabla_{e2}^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

2. a) In the Heitler-London treatment of the H_2 molecule, the wave function

$$\psi_1 = 1s_A(1)1s_B(2)$$

with electron 1 in the $1s$ orbital centered on proton A and electron 2 in the $1s$ orbital centered on proton B was recognized to be unacceptable. Why? Similar consideration apply to the wave function

$$\psi_2 = 1s_A(2)1s_B(1)$$

b) An acceptable wave function is obtained by taking linear combinations of ψ_1 and ψ_2

$$\psi = c_1\psi_1 + c_2\psi_2$$

Why?

c) Minimizing the variational energy leads to the secular equation

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0$$

with

$$S_{12} = S_{21} = S^2 = \int 1s_A(1)1s_B(1) d\tau_1 \int 1s_A(2)1s_B(2) d\tau_2 = (\int 1s_A(1)1s_B(1) d\tau_1)^2$$

$$H_{11} = H_{22} = -1 + J = -1 + \int 1s_A(1)1s_A(1) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \right) 1s_B(2)1s_B(2) d\tau_1 d\tau_2$$

$$H_{12} = H_{21} = -S^2 + K = -S^2 + \int 1s_A(1)1s_B(1) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \right) 1s_A(2)1s_B(2) d\tau_1 d\tau_2$$

Derive an expression for the ground-state energy E_+ . Show that the ground-state wave function is symmetrical ($c_1 = c_2$) and

$$\psi_+ = \frac{1}{\sqrt{2(1+S^2)}}(\psi_1 + \psi_2)$$

d) Derive an expression for the excited-state energy E_- . Show that the corresponding wave function is asymmetrical ($c_1 = -c_2$) and

$$\psi_- = \frac{1}{\sqrt{2(1-S^2)}}(\psi_1 - \psi_2)$$

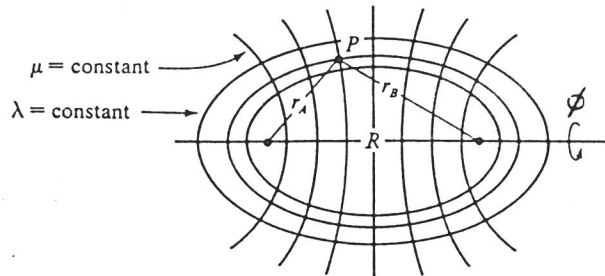
3. Show that the important exchange integral responsible for bond formation arises in the Heitler-London treatment of the H_2 molecule only because the wave function that is used is consistent with the quantum mechanical principle that electrons are indistinguishable.

4. The overlap integral and related integrals that arise in problems such as the H_2 molecule and other diatomics are called **two-center integrals**, for obvious reasons. The easiest way to evaluate two-center integrals is to use **elliptic coordinates**. In this coordinate system, there are two fixed reference points separated by the distance R . The location of point P in three-dimensional space (refer to the diagram) is given by the three elliptic coordinates

$$\lambda = \frac{r_A + r_B}{R}$$

$$\mu = \frac{r_A - r_B}{R}$$

and the angle ϕ of rotation of the r_A, r_B, R triangle about the R axis (called the interfocal axis).



The differential volume element in elliptic coordinates is

$$d\tau = \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

- a) Given the above definitions, show that

$$1 \leq \lambda \leq \infty$$

$$-1 \leq \mu \leq 1$$

$$0 \leq \phi \leq 2\pi$$

- b) Use elliptic coordinates to show that the overlap integral

$$S = \int |s_A| |s_B| d\tau = \frac{Z^3}{\pi} \int e^{-Zr_A} e^{-Zr_B} d\tau$$

is given by the expression

$$S(R) = e^{-ZR} \left(1 + ZR + \frac{Z^2 R^2}{3} \right)$$

5. The Heitler-London ground-state energy of the H₂ molecule is

$$E_+ = 2E_{1s} \left(1 + \frac{J + K}{1 + S^2} \right)$$

J , K , and S are the Coulomb, exchange and overlap integrals discussed in class. In atomic units, the energy is

$$E_+ = -1 + \frac{J + K}{1 + S^2}$$

Show that the Heitler-London energy for the ground-state hydrogen molecule, in atomic units, can be written as

$$E_+ = -1 + \frac{J + \langle ab|ab \rangle - 2S\langle a|ab \rangle + (S^2/R)}{1 + S^2}$$

where

$$\langle ab|ab \rangle = \iint 1s_A(1)1s_B(1) \frac{1}{r_{12}} 1s_A(2)1s_B(2) d\tau_1 d\tau_2$$

$$\langle a|ab \rangle = \iint 1s_A(1)1s_B(1) \frac{1}{r_{A1}} d\tau_1$$

Why do this? It is an instructive way to write the energy of the H₂ molecule because, numerically, the $-2S\langle a|ab \rangle$ term, which is proportional to the overlap integral S , is predominantly responsible for the stability of the H₂ molecule. The larger the value of S , the greater the stability of the molecule. This is the origin of the intuitive idea that greater overlap of orbitals leads to stronger chemical bonds.

6. The ground-state electronic configurations of the O₂ and N₂ molecules are

$$\text{N}_2 \quad (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4 (\sigma 2p_z)^2$$

$$\text{O}_2 \quad (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p)^4 (\sigma 2p_z)^2 (\pi^* 2p)^2$$

Use MO theory to explain why the dissociation energy of N₂ is greater than that of N₂⁺, but the dissociation of O₂ is less than that of O₂⁺.

7. a) Show that the Slater determinantal wave function for the ground-state lithium atom is

$$\begin{aligned} \psi = & \frac{1}{\sqrt{3!}} [1s(1)1s(2)2s(3) - 2s(1)1s(2)1s(3)] \alpha(1)\beta(2)\alpha(3) \\ & + \frac{1}{\sqrt{3!}} [1s(1)2s(2)1s(3) - 1s(1)1s(2)2s(3)] \beta(1)\alpha(2)\alpha(3) \\ & + \frac{1}{\sqrt{3!}} [2s(1)1s(2)1s(3) - 1s(1)2s(2)1s(3)] \alpha(1)\alpha(2)\beta(3) \end{aligned}$$

b) Show that ψ is an eigenfunction of \hat{S}_z

c) What is the eigenvalue?

① a) the energy (in Joules) of a hydrogen-like (one-electron) atom in its ground state ($n=1$) is

$$E_1 = - \frac{m_e c^4 z^2}{8 \epsilon_0^2 h^2 (1)^2}$$

multiply by $\frac{\text{au for energy}}{\text{J}}$

$$E_1 = - \frac{m_e c^4 z^2}{8 \epsilon_0^2 h^2} \frac{1}{\frac{m_e c^4}{(4\pi\epsilon_0)^2 h^2}}$$

to convert to atomic units

$$1 \text{ au} = \frac{m_e c^4}{(4\pi\epsilon_0)^2 h^2}$$

↑ includes

$$E_1 = - \frac{\mu}{m_e} z^2 \frac{1}{\frac{8 h^2}{16\pi^2} \frac{4\pi^2}{h^2}} = - \frac{\mu}{m_e} \frac{z^2}{2} \quad (\text{in au})$$

for $z=2$ (He^+):

$$\frac{\mu}{m_e} = \frac{m_e m_{\text{He}}}{m_e + m_{\text{He}}} \frac{1}{m_e} = \frac{m_{\text{He}}}{m_e + m_{\text{He}}} = \frac{4.0026 \times 1.673 \times 10^{-27}}{9.110 \times 10^{-31} + 4.0026 \times 1.673 \times 10^{-27}}$$

$$= 0.9999 \approx 1 \quad (\text{because electrons are so light})$$

$$E_1 = - \frac{\mu}{m_e} \frac{z^2}{2} \approx (-1) \frac{2^2}{2} = -2 \text{ au}$$

b) $c = 2.998 \times 10^8 \text{ m s}^{-1}$ in SI units

$$c = 2.998 \times 10^8 \frac{\text{m}}{\text{s}} \frac{\frac{\text{au length}}{\text{m}}}{\frac{\text{au time}}{\text{s}}} = 2.998 \times 10^8 \frac{\text{au}}{\text{s}} \frac{5.29177 \times 10^{-11} \text{ m}}{2.4189 \times 10^{-17} \text{ s}}$$

$$= 137.0 \frac{\text{au length}}{\text{au time}} = 137.0 \text{ au speed}$$

(1 cont.)

$$c) \quad r_{au} = \frac{r}{a_0} \quad \psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0} \right)^{3/2} e^{-zr/a_0} \quad \text{SI units}$$

notice that ψ_{1s} has SI units $m^{-3/2}$
(required so that $\int \psi_{1s}^* \psi_{1s} d\tau = 1$ (dimensionless))

$\int \psi_{1s}^* \psi_{1s} d\tau = 1$
 $\psi_{1s}^* \sim m^{-3/2}$, $\psi_{1s} \sim m^{-3/2}$, $d\tau \sim m^3$

$$\psi_{1s} \text{ in au} = \left(\psi_{1s} \text{ in SI units} \right) a_0^{3/2}$$
$$= \sqrt{\frac{z^3}{\pi}} e^{-zr_{au}}$$

$$d) \quad \frac{\hbar^2}{2m_e} \text{ has SI units } \frac{(\text{angular momentum})^2}{\text{mass}}$$

to convert to au, divide by the SI value of the au for angular momentum squared (\hbar^2) and multiply by the SI value of the au for mass (m_e)

$$\frac{\hbar^2}{2m_e} \text{ (SI)} \rightarrow \frac{\hbar^2}{2m_e} \frac{m_e}{\hbar^2} = \frac{1}{2} \text{ in au}$$

similarly, $\frac{e^2}{4\pi\epsilon_0 r}$ is converted to au by dividing by the

au for charge squared (e^2), multiplying by the SI value of the au for $4\pi\epsilon_0$, multiplying by the SI value for the au of length

(1 of cont.)

$$\frac{e^2}{4\pi\epsilon_0 r_{1A}} \text{ (SI)} \rightarrow \frac{e^2}{4\pi\epsilon_0 r_{1A}} \frac{1}{e^2} 4\pi\epsilon_0 a_0 = \frac{1}{r_{1A}/a_0} = \frac{1}{r_{1A} \text{ au}}$$

$$\frac{e^2}{4\pi\epsilon_0 r_{1B}} \text{ (SI)} \rightarrow \frac{1}{r_{1B} \text{ au}} \text{ etc}$$

$$\text{so } \hat{H}_e \text{ (in au)} = -\frac{1}{2} (\nabla_{e1}^2 + \nabla_{e2}^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

② a) The wave function $\psi_1 = 1s_A(1)1s_B(2)$ is unacceptable

because it implies that electron "1" is in the $1s$ orbital centered on proton A and that electron "2" is in the $1s$ orbital centered on proton B, when in fact the electrons can't be labeled "1" or "2". Electrons are indistinguishable.

If electrons 1 and 2 are interchanged, we should have

i) the same wave function (which can be multiplied by an antisymmetric spin function) or ii) the antisymmetric wave function (which can be multiplied by a symmetric spin function)

Interchanging electrons 1 and 2 in $1s_A(1)1s_B(2)$ gives neither i or ii.

$$\text{b) } c_1 = c_2 \text{ (symmetric)} \quad \psi = c_1 (1s_A(1)1s_B(2) + 1s_A(2)1s_B(1))$$

interchange electrons 1 and 2, get:

$$\text{Same wave function} \quad \psi = c_1 (1s_A(2)1s_B(1) + 1s_A(1)1s_B(2))$$

(OK)

(2 b cont.)

$$c_1 = -c_2$$

$$\psi = c_1 (|s_A(1) s_B(2) - |s_A(2) s_B(1)|)$$

interchanging electrons 1 and 2 gives

$$c_1 (|s_A(2) s_B(1) - |s_A(1) s_B(2)|) = -\psi$$

(OK)

$$c) \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} -1 + J - E & -S^2 + K - ES^2 \\ -S^2 + K - ES^2 & -1 + J - E \end{vmatrix} = 0$$

$$(-1 + J - E)^2 - (-S^2 + K - ES^2)^2 = 0$$

$$-1 + J - E = \pm (-S^2 + K - ES^2)$$

$$\text{or } E + 1 - J = \pm (-S^2 + K - ES^2)$$

+

$$E + 1 - J = -S^2 + K - ES^2$$

$$E + ES^2 = -1 - S^2 + J + K$$

$$E_+ = \frac{-1 + J + K}{1 + S^2}$$

-

$$E + 1 - J = -(-S^2 + K - ES^2)$$

$$E - ES^2 = -1 + J + S^2 - K$$

$$E(1 - S^2) = -(1 - S^2) + J - K$$

$$E_- = -1 + \frac{J - K}{1 - S^2}$$

(2 cont.)

$$\underline{E_+} \quad c_1(H_{11} - \frac{E_+ S_{11}}{+}) + c_2(H_{12} - \frac{E_+ S_{12}}{+}) = 0$$

$$c_1(-1+J - E_+) + c_2(-S^2+K - E_+ S^2) = 0$$

$$c_1 \left[-1+J - \left(-1 + \frac{J+K}{1+S^2} \right) \right] + c_2 \left[-S^2+K - S^2 \left(-1 + \frac{J+K}{1+S^2} \right) \right] = 0$$

$$c_1 \left(J - \frac{J+K}{1+S^2} \right) + c_2 \left(K - S^2 \frac{J+K}{1+S^2} \right) = 0$$

$$c_1 \frac{J(1+S^2) - J - K}{1+S^2} + c_2 \frac{K(1+S^2) - S^2 J - S^2 K}{1+S^2} = 0$$

$$c_1 \frac{JS^2 - K}{1+S^2} + c_2 \frac{K - S^2 J}{1+S^2} = 0$$

$$c_1 - c_2 = 0$$

$$c_1 = c_2 \text{ for } E_+ \text{ and } \psi_+$$

$$\psi_+ = c_1 \psi_1 + c_2 \psi_2 = c_1 (\psi_1 + \psi_2)$$

c_1, ψ_1, ψ_2
are real

$$1 = \int \psi_+^* \psi_+ d\tau = \int [c_1(\psi_1 + \psi_2)]^* (c_1 \psi_1 + c_1 \psi_2) d\tau$$

$$= c_1^2 \left[\int \psi_1 \psi_1 d\tau + 2 \int \psi_1 \psi_2 d\tau + \int \psi_2 \psi_2 d\tau \right]$$

$$= c_1^2 \left[\int |s_A^2(1)| |s_B^2(2)| d\tau + 2 \int |s_A(1)| |s_B(2)| |s_A(2)| |s_B(1)| d\tau + \int |s_A^2(2)| |s_B^2(1)| d\tau \right]$$

$$= c_1^2 \left[\int |s_A^2(1)| d\tau_1 \int |s_B^2(2)| d\tau_2 + 2 \int |s_A(1)| |s_B(1)| d\tau_1 \int |s_B(2)| |s_A(2)| d\tau_2 + \int |s_B^2(1)| d\tau_1 \int |s_A^2(2)| d\tau_2 \right]$$

$$1 = c_1^2 [(1)(1) + 2SS + (1)(1)] \quad c_1 = \frac{1}{\sqrt{2(1+S^2)}}$$

③ If we ignore the fact that electrons 1 and 2 are indistinguishable

$\psi = 1s_A(1) 1s_B(2)$ is our trial wave function

variational energy $E' = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (\psi^* = \psi)$

in atomic units:

$$\hat{H}\psi = \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \right] 1s_A(1) 1s_B(2)$$

notice that $\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1A}} \right] 1s_A(1) = E_{1s_{\text{an}}} 1s_A(1) = -\frac{1}{2} 1s_A(1)$

$$\left[-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2B}} \right] 1s_B(2) = -\frac{1}{2} 1s_B(2)$$

so

$$\int \psi^* \hat{H} \psi d\tau = \int 1s_A(1) 1s_B(2) \hat{H} 1s_A(1) 1s_B(2) d\tau$$

$$= \int 1s_A(1) 1s_B(2) \left(-\frac{1}{2} - \frac{1}{2} \right) 1s_A(1) 1s_B(2) d\tau$$

$$+ \int 1s_A(1) 1s_B(2) \left[-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \right] 1s_A(1) 1s_B(2) d\tau$$

$$= \left(-\frac{1}{2} - \frac{1}{2} \right) \int 1s_A^2(1) d\tau_1 \int 1s_B^2(2) d\tau_2 + \int 1s_A^2(1) 1s_B^2(2) \left[\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \right] d\tau$$

$$= (-1)(1)(1) + J$$

$$\int \psi^* \psi d\tau = \int 1s_A(1) 1s_B(2) 1s_A(1) 1s_B(2) d\tau = \int 1s_A^2(1) d\tau_1 \int 1s_B^2(2) d\tau_2 = 1$$

$$E' = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} = \frac{-1+J}{1} \quad \text{no exchange integral K!}$$

④ a) $\lambda = \frac{r_A + r_B}{R}$ $r_A + r_B$ can never be less than R ,
and so $\lambda \geq 1$

$$\mu = \frac{r_A - r_B}{R}$$

the difference $r_A - r_B$ can never exceed $\pm R$ (colinear case)

and so $-1 \leq \mu \leq 1$

ϕ can rotate through 360° , and so $0 \leq \phi \leq 2\pi$

b) $S = \int |S_A(i)| |S_B(i)| d\tau,$

$$= \int \sqrt{\frac{z^3}{\pi}} e^{-zr_A} \sqrt{\frac{z^3}{\pi}} e^{-zr_B} d\tau$$

$$= \frac{z^3}{\pi} \int e^{-zr_A} e^{-zr_B} d\tau$$

$$r_A + r_B = \lambda R$$

$$= \frac{z^3}{\pi} \iiint e^{-z(r_A + r_B)} \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

$$= \frac{z^3}{\pi} \frac{R^3}{8} \int_0^{2\pi} \int_0^1 \int_0^1 e^{-z\lambda R} (\lambda^2 - \mu^2) d\lambda d\mu d\phi$$

$$= \frac{z^3}{\pi} \frac{R^3}{8} \left[\int_0^1 \int_0^1 (\lambda^2 e^{-z\lambda R} - \mu^2 e^{-z\lambda R}) d\lambda d\mu \right] 2\pi$$

$$= \frac{z^3 R^3}{4} \int_0^1 e^{-z\lambda R} \left[\int_{\mu=-1}^1 (\lambda^2 - \mu^2) d\mu \right] d\lambda = \frac{z^3 R^3}{4} \int_0^1 e^{-z\lambda R} \left(\lambda^2 - \frac{\mu^3}{3} \right) \Big|_{\mu=-1}^{\mu=1} d\lambda$$

$$= \frac{z^3 R^3}{4} \int_0^1 e^{-z\lambda R} \left(\lambda^2 - \frac{2}{3} \right) d\lambda$$

(4 b cont.)

$$\int x^2 e^{-x} dx = -e^{-x} [2 + 2x + x^2]$$

$$S = \frac{z^3 R^3}{2} \int \lambda^2 e^{-z\lambda R} d\lambda - \frac{z^3 R^3}{6} \int e^{-z\lambda R} d\lambda$$

$$= \frac{z^3 R^3}{2} \frac{1}{(zR)^3} \int_{zR}^{\infty} (zR\lambda)^2 e^{-z\lambda R} d(z\lambda R) - \frac{z^3 R^3}{6} \frac{1}{zR} \int_{zR}^{\infty} e^{-z\lambda R} d(z\lambda R)$$

$$= \frac{1}{2} \int_{zR}^{\infty} \varphi^2 e^{-\varphi} d\varphi - \frac{z^2 R^2}{6} \int_{zR}^{\infty} e^{-\varphi} d\varphi$$

$$= \frac{1}{2} \left[-e^{-\varphi} (2 + 2\varphi + \varphi^2) \right] \Big|_{\varphi=zR}^{\infty} + \frac{z^2 R^2}{6} \left(-e^{-\varphi} \right) \Big|_{zR}^{\infty}$$

$$= \frac{1}{2} e^{-zR} (2 + 2zR + z^2 R^2) - \frac{z^2 R^2}{6} e^{-zR}$$

$$S = e^{-zR} \left(1 + zR + \frac{z^2 R^2}{3} \right)$$

⑤

$$E_+ = -1 + \frac{J+K}{1+S^2}$$

in atomic units

exchange integral $K = \int \psi_A(1) \psi_B(2) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \right) \psi_B(1) \psi_A(2) d\tau_1 d\tau_2$

$$K = \int \psi_A(2) \psi_B(2) d\tau_2 \int \frac{\psi_A(1) \psi_B(1)}{r_{1A}} d\tau_1 - \int \psi_A(1) \psi_B(1) d\tau_1 \int \frac{\psi_A(2) \psi_B(2)}{r_{2B}} d\tau_2$$

$$+ \int \frac{\psi_A(1) \psi_B(1) \psi_A(2) \psi_B(2)}{r_{12}} d\tau_1 d\tau_2 + \frac{1}{R} \int \psi_A(1) \psi_B(1) d\tau_1 \int \psi_A(2) \psi_B(2) d\tau_2$$

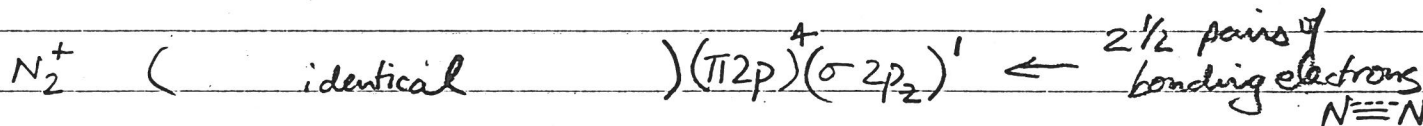
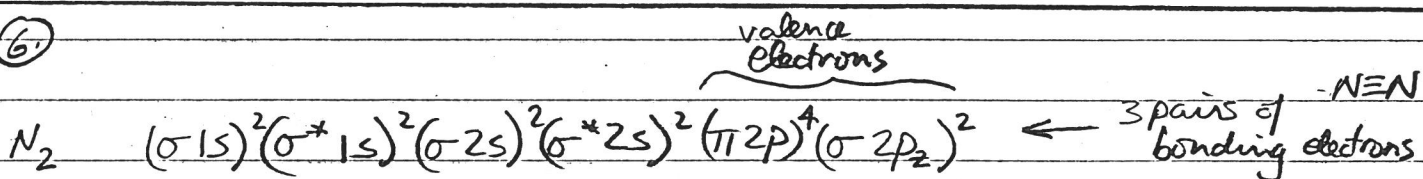
(5 cont.)

$$K = -S\langle a|ab\rangle - S\langle a|ab\rangle + \langle ab|ab\rangle + \frac{S^2}{R}$$

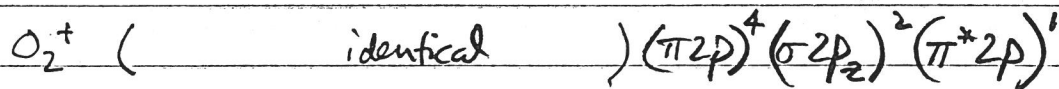
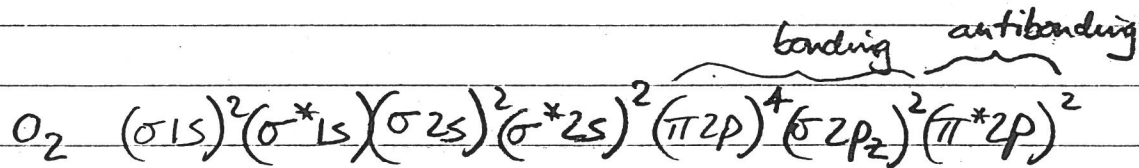
$$E_+ = -1 + \frac{J+K}{1+S^2} = -1 + \frac{J - 2S\langle a|ab\rangle + \langle ab|ab\rangle + \frac{S^2}{R}}{1+S^2}$$

the larger the overlap integral S , the more negative E_+ becomes \Rightarrow more stable H_2 molecule

(6)



\therefore dissociation energy of $N_2 >$ that of N_2^+



O_2 has 4 + 2 bonding electrons and 2 antibonding electrons
net 4 bonding electrons (double bond) $O=O$

O_2^+ has 4 + 2 - 1 = 5 net bonding electrons $O \equiv O^+$

$\therefore O_2^+$ has a higher dissociation energy than O_2

⑦ The Slater determinantal wave function (combining spatial and spin factors) for ground-state Li atoms:

$$a) \quad \psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

(rows \rightarrow same electron, different spin orbitals
 columns \rightarrow same spin orbital, different electrons
 the 3rd column could also be $2s\beta(1), 2s\beta(2), 2s\beta(3)$)

$$\psi = \frac{1}{\sqrt{6}} [1s\alpha(1) 1s\beta(2) 2s\alpha(3) - 1s\alpha(1) 1s\beta(3) 2s\alpha(2) \\ - 1s\beta(1) 1s\alpha(2) 2s\alpha(3) + 1s\beta(1) 1s\alpha(3) 2s\alpha(2) \\ + 2s\alpha(1) 1s\alpha(2) 1s\beta(3) - 2s\alpha(1) 1s\alpha(3) 1s\beta(2)]$$

$$b) \quad \hat{S}_z = \hat{S}_{z\text{total}} = \hat{S}_{z1} + \hat{S}_{z2} + \hat{S}_{z3}$$

$$\text{for electron } i, \quad \hat{S}_{zi} \alpha(i) = \frac{\hbar}{2} \alpha(i)$$

$$\hat{S}_{zi} \beta(i) = -\frac{\hbar}{2} \beta(i)$$

the eigenvalues of \hat{S}_{zi} are $\pm \frac{\hbar}{2}$

(7 cont.)

$$\hat{S}_z \psi = (\hat{S}_{z1} + \hat{S}_{z2} + \hat{S}_{z3}) \psi$$

$$= \frac{1}{\sqrt{6}} \left[\frac{\hbar}{2} (-1+1+1) 1s\alpha(1) 1s\beta(2) 2s\alpha(3) - \frac{\hbar}{2} (1-1+1) 1s\alpha(1) 1s\beta(3) 2s\alpha(2) \right.$$

$$\left. - \frac{\hbar}{2} (-1+1+1) 1s\beta(1) 1s\alpha(2) 2s\alpha(3) + \frac{\hbar}{2} (-1+1+1) 1s\beta(1) 1s\alpha(3) 2s\alpha(2) \right.$$

$$\left. + \frac{\hbar}{2} (1+1-1) 2s\alpha(1) 1s\alpha(2) 1s\beta(3) - \frac{\hbar}{2} (1+1-1) 2s\alpha(1) 1s\alpha(3) 1s\beta(2) \right]$$

$$\hat{S}_z = \frac{\hbar}{2} \psi$$

c) eigenvalue $\frac{\hbar}{2}$ $\left(\frac{1}{2} \text{ in atomic units} \right)$