Printed Pages – 8 Roll No. : ....

Corrected copy

AS-2161

M. Sc. (Third Semester) Examination, 2013

CHEMISTRY

Paper : CMT-304 (P)

(Specialization-Physical Chemistry)

(Quantum Chemistry)

Time Allowed : Three hours

Maximum Marks : 60

Note : *Question no. 1 from Section-'A' is compulsory. Solve any* ***five*** *questions from Section–'B'.*

Section-'A' 10×2=20

Note : *Attempt all the questions. Each question carries 2 marks.*

1. Choose the correct answer :

(i) Uncertainty principle states that the error in measurement is due to :

(a) dual nature of particles

(b) due to small size of particles

(c) due to large size of particles

(d) due to error in measuring instrument

(ii) The solution to the Schrödinger equation for a particle bound in a one-dimensional, infinitely deep potential well, indexed by quantum number n, indicates that in the middle of the well the probability density vanishes for :

(a) the ground state $(n = 1)$ only

(b) states of even $n\,(n = 2, 4, ...)$

(c) states of odd $n\,(n = 1, 3, ...)$

(d) all states except the ground state

$\hat{p}_x$

(iii) $\left[\hat{z}, \widehat{px}\right] = ...$:

(a) $-i\hbar\hat{I}$

(b) 0

(c) $i\hbar\hat{I}$

(d) none of the above

(iv) Energy eigen values of SHO are :

(a) $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$,where ω is the angular frequency $\omega = \sqrt{\frac{k}{m}}$

(b) $E_n = (2n + 1)\,E_0$, where E_0 is the ground state energy, n = quantum number

(c) The energy levels are evenly or equally spaced witha constant energy difference of $\frac{1}{2}\hbar\omega$

with a

(d) The energy value is always an odd multiple of $\hbar\omega$

(v) $\delta_{ij} = 0$, when :

(a) $i > j$

(b) $i < j$

(c) $i \neq j$

(d) $i = j$

(vi) The number operator $\widehat{N} = \hat{a}^{\dagger}\hat{a}$ is :

(a) Hermitian

(b) Anti-Hermitian

(c) Symmetric

(d) None of the above

(vii) The electronic energy levels of atoms of a certain gas are given by $E_n = E_1 n^2$, where $n = 1, 2, 3, \ldots$ Assume that transitions are allowed between all levels. If one wanted to construct a LASER from this gas by pumping the $n = 1 \rightarrow n = 3$ transition, which energy level or levels would have to be metastable :

(a) $n = 1$ only

(b) $n = 2$ only

(c) $n = 1$ and $n = 3$ only

(d) $n = 1$, $n = 2$ and $n = 3$

(viii) The Russel-Saunders terms for d^1 :

(a) ${}^2D_{5/2}$, ${}^2D_{3/2}$

(b) ${}^2D_{5/2}$, ${}^2P_{3/2}$

(c) only ${}^2D_{5/2}$

(d) only ${}^2D_{3/2}$

(ix) The ionization energy of hydrogen atom :

(a) −13·6 eV

(b) 13·6 eV

(c) 0 eV

(d) infinite

(x) Consider a 4-fold degenerate state with orthonormal eigen functions u_1, u_2, u_3, u_4. There is a perturbation H'. It is given that

$H'_{12} = H'_{21} = -g; g > 0$ and all the other matrix elements are zero. Find the spliting :

(a) $g, -g, 0, 0$

(b) $2g, g, 0, 0$

(c) $g, g, 0, 0$

(d) $g, 0, 0, 0$

AS-2161
M.Sc. (Third Sem) Examination, 2013
Chemistry (Specialization - Physical Chemistry)

Quantum Chemistry

Section - A

1. (i) (a) (ii) (b) (iii) (b) (iv) (a) (v) (c)
(vi) (a) (vii) (b) (viii) (a) (ix) (b) (x) (a)

Section - B

2. 'Ladder operators', also called "raising" and "lowering" operators are defined as $\hat{J}_+ = \hat{J}_x + i\hat{J}_y$; $\hat{J}_- = \hat{J}_x - i\hat{J}_y$.

(i) Show that $\hat{J}^2 = \hat{J}_+\hat{J}_- + \hat{J}_z^2 - \hbar\hat{J}_z$ and

$$\hat{J}^2 = \hat{J}_-\hat{J}_+ + \hat{J}_z^2 + \hbar\hat{J}_z$$

(ii) Show that $\hat{J}_z\hat{J}_\pm = \hat{J}_\pm(\hat{J}_z \pm \hbar)$

Ans (i)
$$\hat{J}_+\hat{J}_- = (\hat{J}_x + i\hat{J}_y)(\hat{J}_x - i\hat{J}_y)$$
$$= \hat{J}_x^2 + \hat{J}_y^2 + i\hat{J}_y\hat{J}_x - i\hat{J}_x\hat{J}_y$$
$$= \hat{J}_x^2 + \hat{J}_y^2 - i[\hat{J}_x, \hat{J}_y]$$
$$= \hat{J}^2 - \hat{J}_z^2 - i(i\hbar\hat{J}_z)$$
$$= \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z$$

or, $\hat{J}^2 = \hat{J}_+\hat{J}_- + \hat{J}_z^2 - \hbar\hat{J}_z$

Similarly
$$\hat{J}_-\hat{J}_+ = (\hat{J}_x - i\hat{J}_y)(\hat{J}_x + i\hat{J}_y)$$
$$= \hat{J}_x^2 + \hat{J}_y^2 + i[\hat{J}_x, \hat{J}_y]$$
$$= \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$$

or, $\hat{J}^2 = \hat{J}_-\hat{J}_+ + \hat{J}_z^2 + \hbar\hat{J}_z$

(ii)
$$\hat{J}_z\hat{J}_\pm = \hat{J}_z(\hat{J}_x \pm i\hat{J}_y) = \hat{J}_z\hat{J}_x \pm i\hat{J}_z\hat{J}_y$$
$$= (\hat{J}_z\hat{J}_x - \hat{J}_x\hat{J}_z) + \hat{J}_x\hat{J}_z \pm i(\hat{J}_z\hat{J}_y - \hat{J}_y\hat{J}_z) \pm i\hat{J}_y\hat{J}_z$$
$$= [\hat{J}_z, \hat{J}_x] + \hat{J}_x\hat{J}_z \pm i[\hat{J}_z, \hat{J}_y] \pm i\hat{J}_y\hat{J}_z$$

$$= i\hbar\hat{J}_y + \hat{J}_x\hat{J}_z \pm i(-i\hbar\hat{J}_x) \pm i\hat{J}_y\hat{J}_z$$

$$= (i\hbar\hat{J}_y \pm \hbar\hat{J}_x) + (\hat{J}_x\hat{J}_z \pm i\hat{J}_y\hat{J}_z)$$

$$= \pm\hbar(\hat{J}_x \pm i\hat{J}_y) + (\hat{J}_x \pm i\hat{J}_y)\hat{J}_z$$

$$= \pm\hbar\hat{J}_\pm + \hat{J}_\pm\hat{J}_z \quad = \hat{J}_\pm(\hat{J}_z \pm \hbar)$$

3. Calculate the uncertainty product $\Delta r\Delta p_r$ in the ground state of the hydrogen atom.

Ans In atomic unit, the ground state wave function

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}}e^{-r}$$

Now $\Delta r = \sqrt{\langle r^2\rangle - \langle r\rangle^2}$ and $\Delta p_r = \sqrt{\langle p_r^2\rangle - \langle p_r\rangle^2}$

$$\langle r\rangle = \int_0^\infty r\left(\frac{1}{\sqrt{\pi}}e^{-r}\right)^2 4\pi r^2 dr = 4\int_0^\infty e^{-2r}r^3 dr = 4\times\frac{3!}{2^4} = \frac{3}{2}$$

$$\langle r^2\rangle = \int_0^\infty r^2\left(\frac{1}{\sqrt{\pi}}e^{-r}\right)^2 4\pi r^2 dr = 4\int_0^\infty e^{-2r}r^4 dr = 4\times\frac{4!}{2^5} = 3$$

The radial momentum operator is defined by

$$\hat{p}_r = -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r$$

$$\therefore \langle p_r\rangle = \int_0^\infty \frac{1}{\sqrt{\pi}}e^{-r}\left\{-i\hbar\frac{1}{r}\frac{\partial}{\partial r}r\right\}\frac{1}{\sqrt{\pi}}e^{-r}4\pi r^2 dr$$

$$= -4i\hbar\int_0^\infty e^{-r}\frac{1}{r}(e^{-r} - re^{-r})r^2 dr = -4i\hbar\left(\frac{1!}{2^2} - \frac{2!}{2^3}\right) = 0$$

$$\langle p_r^2\rangle = \int_0^\infty \frac{1}{\sqrt{\pi}}e^{-r}\left\{-\cancel{i}\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right\}\frac{1}{\sqrt{\pi}}e^{-r}4\pi r^2 dr$$

$$= \hbar^2$$

$$\therefore \Delta r = \sqrt{3 - \left(\frac{3}{2}\right)^2} = \frac{\sqrt{3}}{2} \quad \text{and} \quad \Delta p_r = \sqrt{\hbar^2 - 0} = \hbar$$

$$\therefore \Delta r\Delta p_r = \frac{\sqrt{3}}{2}\hbar > \frac{\hbar}{2}.$$

4. Evaluate the average (expectation) values of potential energy and kinetic energy for the ground state of the harmonic oscillator. Comment on the relative magnitude of these two quantities.

Ans We know $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(\hat{a}+\hat{a}^{+})$

$$\hat{p} = \frac{1}{i}\sqrt{\frac{m\omega\hbar}{2}}\,(\hat{a}-\hat{a}^{+})$$

$$\therefore \langle \hat{x}^2 \rangle = \frac{\hbar}{2m\omega}\langle n|(\hat{a}+\hat{a}^{+})(\hat{a}+\hat{a}^{+})|n\rangle$$

$$= \frac{\hbar}{2m\omega}\langle n|(\hat{a}\hat{a}+\hat{a}^{+}\hat{a}^{+}+\hat{a}\hat{a}^{+}+\hat{a}^{+}\hat{a})|n\rangle$$

$$= \frac{\hbar}{2m\omega}(0+0+(n+1)+n) = \frac{\hbar}{2m\omega}(2n+1)$$

$\therefore$ For ground state

$$\langle \hat{x}^2 \rangle = \frac{\hbar}{2m\omega} \quad \text{and}$$

$$\langle P.E. \rangle = \langle V \rangle = \frac{1}{2}m\omega^2\langle \hat{x}^2 \rangle = \frac{1}{4}\hbar\omega$$

Similarly $\langle \hat{p}^2 \rangle = \frac{\hbar m\omega}{2}(2n+1)$

$$= \frac{1}{2}\hbar m\omega \text{ for ground state}$$

$$\therefore \langle K.E. \rangle = \frac{1}{2m}\langle \hat{p}^2 \rangle = \frac{1}{4}\hbar\omega \text{ for ground state.}$$

Hence $\langle K.E. \rangle = \langle P.E. \rangle = \frac{1}{2} \times$ ground state energy.

The average values of potential and kinetic energies for the harmonic oscillator are equal. This is an instance of the virial theorem, which states that for a potential energy of the form

$$V(x) = \text{Const.} \times x^n,$$

the average kinetic and potential energies are related by

$$2\langle K.E. \rangle = n\langle P.E. \rangle$$

5. For non-degenerate energy levels by using perturbation theory derive the expression for the first-order correction to the wave function.

Ans Assume the unperturbed Schrödinger equation is given by $\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, where ——— ①

$\psi_n^{(0)}$ = wave function of unperturbed nondegenerate level with energy $E_n^{(0)}$.

Let ψ_n is the perturded wave function and the perturbed Schrodinger eqn. is given by

$$\hat{H}\psi_n = (\hat{H}^0 + \lambda\hat{H}')\psi_n = E_n\psi_n$$ ——— ②

Since the perturbed Hamiltonian $\hat{H}$ is a function of λ (parameter), both ψ_n and E_n will depend on λ; i.e.

$$\psi_n = \psi_n(\lambda, q), \quad q = \text{system's coordinates}$$

$$E_n = E_n(\lambda).$$

By using Taylor-series expansion, we can write

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots\cdots$$ ——— ③

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\cdots$$ ——— ④

Substituting ③ & ④ into ③,

$$(\hat{H}^0 + \lambda\hat{H}')(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots\cdots)$$
$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\cdots)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots\cdots)$$

or, $$\hat{H}^0\psi_n^{(0)} + \lambda(\hat{H}'\psi_n^{(0)} + \hat{H}^{(0)}\psi_n^{(1)}) + \lambda^2(\hat{H}^0\psi_n^{(2)} + \hat{H}'\psi_n^{(1)}) + \cdots\cdots$$
$$= E_n^{(0)}\psi_n^{(0)} + \lambda(E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}) + \lambda^2(E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}) + \cdots\cdots$$

Equating the coefficients of λ;

$$\hat{H}^0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \longrightarrow \text{unperturbed Schrödinger eqn.}$$

$$\hat{H}'\psi_n^{(0)} + \hat{H}^0\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}$$ ——— ⑤

$$\hat{H}^0\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}$$

From eqn. ⑤

$$\hat{H}^{0}\psi_n^{(1)} - E_n^{(0)}\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} - \hat{H}'\psi_n^{(0)}$$

Multiply both side by $\psi_m^{(0)*}$ and integrate over all space

$$\langle\psi_m^{(0)}|\hat{H}^{0}|\psi_n^{(1)}\rangle - E_n^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_n^{(1)}\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle - \langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$$

or, $E_m^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle - E_n^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_n^{(1)}\delta_{mn} - \langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$

or, $(E_m^{(0)} - E_n^{(0)})\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_n^{(1)}\delta_{mn} - \langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$ ——— ⑥

For $m \neq n$, $\delta_{mn} = 0$ so,

$(E_m^{(0)} - E_n^{(0)})\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = -\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$ ——— ⑦

Now expand $\psi_n^{(1)}$ in terms of the complete, orthonormal set of unperturbed eigen functions $\psi_m^{(0)}$ of the Hamiltonian operator $\hat{H}^{0}$: $\psi_n^{(1)} = \sum_m a_m \psi_m^{(0)}$ ——— ⑧

where $a_m = \langle\psi_m^{(0)}|\psi_n^{(1)}\rangle$ = expansion coefficient.

So from ⑦

$$(E_m^{(0)} - E_n^{(0)})\, a_m = -\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$$

or, $a_m = \dfrac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$

Putting the value of a_m in ⑧,

$\psi_n^{(1)} = \sum\limits_{m\neq n} \dfrac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}$ ——— ⑨

Setting $\lambda = 1$ in eqn. ③ and using the first-order wave function correction, the perturbed wave function can be written as

$$\psi_n \cong \psi_n^{(0)} + \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\psi_m^{(0)}$$

6. Calculate the ground-state energy of helium atom by using time-independent perturbation theory. Compare the calculated energy with the experimental value.

Ans

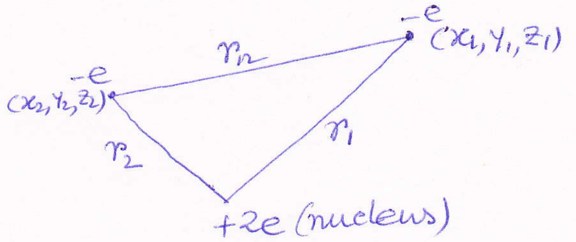

Fig: Interparticle distances in helium atom

Hamiltonian for helium atom is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze'^2}{r_1} - \frac{Ze'^2}{r_2} + \underset{\uparrow \text{ interelectronic repulsion}}{\frac{e'^2}{r_{12}}}, \qquad \text{———} ①$$

$$e' = \frac{e}{\sqrt{4\pi\epsilon_0}}$$

The Schrödinger eqn. involves six independent variables, three coordinates for each electron. In spherical coordinates, the wave function $\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$r_{12} = [(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2]^{1/2}$, express this in terms of spherical coordinates $(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$.

Because of $\frac{1}{r_{12}}$ term in ①, the Schrödinger eqn. can not be separable.

Unperturbed part of the Hamiltonian

$$\hat{H}^0 = \underline{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_1}} \underline{- \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_2}} \qquad \text{———} ②$$

$$= \hat{H}_1^0 + \hat{H}_2^0$$

Perturbed part of the Hamiltonian

$$\hat{H}' = \frac{e'^2}{r_{12}}$$

Here unperturbed system is helium atom in which the two electrons exert no forces on each other. The unperturbed Hamiltonian ② is the sum of the Hamiltonians for two independent particles, so we can apply here the separationof-variables technique. Hence unperturbed wave function

$$\psi^{(0)}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = F_1(r_1,\theta_1,\phi_1)\, F_2(r_2,\theta_2,\phi_2) \quad \text{and} \qquad ③$$

the unperturbed energy

$$E^{(0)} = E_1 + E_2 \quad \text{where } \hat{H}_1^\circ F_1 = E_1 F_1$$
$$\hat{H}_2^\circ F_2 = E_2 F_2$$

Now $E_1 = -\frac{Z^2}{n_1^2}\frac{e^2}{2a_0}$, $n_1 = 1, 2, 3, ----$

$E_2 = -\frac{Z^2}{n_2^2}\frac{e^2}{2a_0}$, $n_2 = 1, 2, 3, -----$

$\therefore E^{(0)} = -Z^2\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)\frac{e^2}{2a_0}$, a_0 = Bohr radius.

$= -Z^2(2)\cdot\frac{e^2}{2a_0}$ for ground state $n_1 = n_2 = 1$

$\therefore E^{(0)}_{1s^2} = -(4)(2).(13.606)$ eV as $Z = 2$ for helium

$= -108.83$ eV (unperturbed energy)

Experimental ground state energy of He $= -79.01$ eV.

Hence unperturbed energy is in error by ~38%.

Now first order perturbation correction to energy

$$E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle$$

Ground state wave function of hydrogen like system

$$\psi^{(0)}_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

So from eqn. ③, zero-order wave function of He (unperturbed)

$$\psi^{(0)}_{1s^2} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_1/a_0} \cdot \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_2/a_0} = 1S(1)\,1S(2)$$

$$\therefore E^{(1)} = \langle \psi^{(0)}_{1s^2} | \hat{H}' | \psi^{(0)}_{1s^2} \rangle$$

$$= \frac{Z^6 e^2}{\pi^2 a_0^6}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{\infty} e^{-2Zr_1/a_0}\, e^{-2Zr_2/a_0}\,\frac{1}{r_{12}}\, r_1^2\sin\theta_1\, r_2^2\sin\theta_2 \times dr_1\, dr_2\, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2$$

or, $E^{(1)} = \frac{5Z}{8}\left(\frac{e^2}{a_0}\right) = \frac{5Z}{4}\left(\frac{e^2}{2a_0}\right)$

$= \frac{5.2}{4}(13.6) = 34.01$ eV.

∴ Energy after first order correction

$= E^{(0)} + E^{(1)} = -108.83\text{ eV} + 34.01\text{ eV}$

$= -74.82$ eV, which is in error by 5.3%.

We know $E^{(2)} \simeq -4.29$ eV

$E^{(3)} \simeq +0.12$ eV.

∴ Upto third order corrections, the ground state energy

$E \cong (-108.83 + 34.01 - 4.29 + 0.12)$ eV

$= -78.99$ eV (theoretical calculation)

$= -79.01$ eV (Expt.)

7. Define Condon-Slater rules. For Be atom, write down the ground state determinantal wave function and the Hamiltonian in atomic unit. Discuss how can you calculate the ground state energy of Be atom in terms of Coulomb and exchange integrals.

Ans Assume $H_{kl} = \langle \Psi_k | \hat{H} | \Psi_l \rangle = \langle \Psi_k | \sum_i \hat{H}_i^{\circ} | \Psi_l \rangle + \langle \Psi_k | \sum_{i<j} \frac{1}{r_{ij}} | \Psi_l \rangle$

where the first term represents 1-electron integrals and the second term 2-electron integrals.

If ϕ_i are the spin-orbitals in the slater determinant Ψ_k and ϕ_i' those in Ψ_l, then the rules take the following form

Ψ_k and Ψ_l differ in	$\langle \Psi_k \vert \sum_i \hat{H}_i^{\circ} \vert \Psi_l \rangle$	$\langle \Psi_k \vert \sum_{i<j} \frac{1}{r_{ij}} \vert \Psi_l \rangle$
1. no spin orbitals	$\sum_i \langle i \vert \hat{H}^{\circ} \vert i \rangle$	$\sum_{i<j} \left[\langle ij \vert \frac{1}{r_{12}} \vert ij \rangle - \langle ij \vert \frac{1}{r_{12}} \vert ji \rangle \right]$
2. One spin-orbitals ($\phi_i \neq \phi_i'$)	$\langle i \vert \hat{H}^{\circ} \vert i' \rangle$	$\sum_{j \neq i} \left[\langle ij \vert \frac{1}{r_{12}} \vert i'j \rangle - \langle ij \vert \frac{1}{r_{12}} \vert ji' \rangle \right]$
3. Two spin-orbitals $\phi_i \neq \phi_i'$	0	$\langle ij \vert \frac{1}{r_{12}} \vert i'j' \rangle - \langle ij \vert \frac{1}{r_{12}} \vert j'i' \rangle$
4. more than two spin-orbitals	0	0

where $\langle i|\hat{H}^\circ|j\rangle = \int \phi_i^*(1)\,\hat{H}^\circ\,\phi_j(1)\,d\tau_1$

$$\langle ij|\frac{1}{r_{12}}|rs\rangle = \int \phi_i^*(1)\,\phi_j^*(2)\,\frac{1}{r_{12}}\,\phi_r(1)\,\phi_s(2)\,d\tau_1\,d\tau_2$$

Ground state wave function for Be

$$\Psi = \frac{1}{\sqrt{4!}}\begin{vmatrix} 1S(1) & \overline{1S}(1) & 2S(1) & \overline{2S}(1) \\ 1S(2) & \overline{1S}(2) & 2S(2) & \overline{2S}(2) \\ 1S(3) & \overline{1S}(3) & 2S(3) & \overline{2S}(3) \\ 1S(4) & \overline{1S}(4) & 2S(4) & \overline{2S}(4 \end{vmatrix}$$

Hamiltonian $\hat{H} = (\hat{H}_1^\circ + \hat{H}_2^\circ + \hat{H}_3^\circ + \hat{H}_4^\circ) + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{34}} + \frac{1}{r_{13}} + \frac{1}{r_{14}} + \frac{1}{r_{24}}$

where $\hat{H}_1^\circ = -\frac{1}{2}\nabla_1^2 - \frac{4}{r_1}$ (Hydrogenlike)

$\hat{H}_2^\circ = -\frac{1}{2}\nabla_2^2 - \frac{4}{r_2}$, etc

Now ground state energy

$$E = \langle\Psi|\hat{H}|\Psi\rangle$$

$$= \langle 1s|\hat{H}_1^\circ|1s\rangle + \langle\overline{1s}|\hat{H}_2^\circ|\overline{1s}\rangle + \langle 2s|\hat{H}_3^\circ|2s\rangle + \langle\overline{2s}|\hat{H}_4^\circ|\overline{2s}\rangle$$

$$+ \langle 1s\,\overline{1s}|\frac{1}{r_{12}}|1s\,\overline{1s}\rangle + \langle 2s\,\overline{2s}|\frac{1}{r_{12}}|2s\,\overline{2s}\rangle + \langle 1s\,2s|\frac{1}{r_{12}}|1s\,2s\rangle$$

$$+ \langle 1s\,\overline{2s}|\frac{1}{r_{12}}|1s\,\overline{2s}\rangle + \langle\overline{1s}\,2s|\frac{1}{r_{12}}|\overline{1s}\,2s\rangle + \langle\overline{1s}\,\overline{2s}|\frac{1}{r_{12}}|\overline{1s}\,\overline{2s}\rangle$$

$$- \langle 1s\,2s|\frac{1}{r_{12}}|2s\,1s\rangle - \langle\overline{1s}\,\overline{2s}|\frac{1}{r_{12}}|\overline{2s}\,\overline{1s}\rangle$$

$$= 2E_{1s}^\circ + 2E_{2s}^\circ + J_{1s1s} + J_{2s2s} + 4J_{1s2s} - 2K_{1s2s}$$

where the terms can be simplifed like

$$\langle 1s|\hat{H}_1^\circ|1s\rangle = \langle 1s|\hat{H}_1^\circ|1s\rangle\langle\alpha|\alpha\rangle = \langle 1s|\hat{H}_1^\circ|1s\rangle$$

$$\langle\overline{1s}|\hat{H}_2^\circ|\overline{1s}\rangle = \langle 1s|\hat{H}_2^\circ|1s\rangle\langle\beta|\beta\rangle = \langle 1s|\hat{H}_2^\circ|1s\rangle$$

Similarly $\langle 1s(1)\,\overline{1s}(2)|\frac{1}{r_{12}}|1s(1)\,\overline{1s}(2)\rangle$

$$= \langle 1s(1)\,1s(2)|\frac{1}{r_{12}}|1s(1)\,1s(2)\rangle\langle\alpha(1)|\alpha(1)\rangle\langle\beta(2)|\beta(2)\rangle$$

$$= \langle 1s\,1s|\frac{1}{r_{12}}|1s\,1s\rangle$$

$$\langle 1s(1)\,\overline{2s}(2)|\frac{1}{r_{12}}|\overline{1s}(1)\,2s(2)\rangle$$

$$= \langle 1s(1)\,2s(2)|\frac{1}{r_{12}}|1s(1)\,2s(2)\rangle\langle\alpha(1)|\beta(1)\rangle\langle\beta(2)|\alpha(2)\rangle$$

$$= 0$$

In this way we have to simplify and finally intigrate to get the energy.

8. Discuss how one can calculate the total electronic energy of helium by Roothaan's method.

Ans The Roothaan equation is given by

$$\sum_{s=1}^{b} C_{si}(F_{rs} - \varepsilon_i S_{rs}) = 0 \qquad ①$$

F_{rs} and S_{rs} integrals we have to evaluate. Let the normalised basis function are given by

$$\chi_1 = 2\zeta_1^{3/2} e^{-\zeta_1 r} Y_0^0$$

$$\chi_2 = 2\zeta_2^{3/2} e^{-\zeta_2 r} Y_0^0$$

where ζ_1 and ζ_2 are the orbital exponent.

The overlap integrals S_{rs} are given by

$$S_{11} = \langle \chi_1 | \chi_1 \rangle = 1$$

$$S_{22} = \langle \chi_2 | \chi_2 \rangle = 1$$

$$S_{12} = S_{21} = \langle \chi_1 | \chi_2 \rangle = 4\zeta_1^{3/2}\zeta_2^{3/2} \int_0^\infty e^{-(\zeta_1+\zeta_2)r} r^2 dr$$

$$= \frac{8\zeta_1^{3/2}\zeta_2^{3/2}}{(\zeta_1+\zeta_2)^3}.$$

F_{rs} is given by

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b}\sum_{j=1}^{n/2} C_{tj}^{*} C_{uj}\left[2(rs|tu) - (ru|ts)\right] \qquad ②$$

and so its depend on H_{rs}^{core}, P_{tu} and $(rs|tu)$.

$$P_{tu} = 2\sum_{j=1}^{n/2} C_{tj}^{*} C_{uj} \qquad ③$$

Now $\hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}}$

$$\therefore \hat{H}^{core} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r}$$

$$\therefore H_{11}^{core} = \langle \chi_1 | \hat{H}^{core} | \chi_1 \rangle$$

$$H_{22}^{core} = \langle \chi_2 | \hat{H}^{core} | \chi_2 \rangle$$

$$H_{12}^{core} = H_{21}^{core} = \langle \chi_1 | \hat{H}^{core} | \chi_2 \rangle$$

We have to solve these three integrals for the 1st term of equation ②.

Many of the electron-repulsion integrals $(rs|tu)$ are equal to one another. For real basis functions, one can show that

$$(rs|tu) = (sr|tu) = (rs|ut) = (sr|ut) = (tu|rs) = (ut|rs) = (tu|sr) = (ut|sr$$

The electron-repulsion integrals are evaluated by using the $\frac{1}{r_{12}}$ expansion,

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} \left[Y_l^m(\theta_1, \phi_1)\right]^* Y_l^m(\theta_2, \phi_2)$$

We have to evaluate sixteen electron-repulsion integrals $(rs|tu)$ like, $(11|11)$, $(22|22)$, $(11|22)$, $(12|12)$, $(11|12)$, $(12|22)$ etc.

To start the calculation, we need an initial guess for the ground state AO expansion coefficients c_{si} in

$$\phi_i = \sum_{s=1}^{b} c_{si} \chi_s$$

so that we can get an initial estimate of the density matrix elements P_{tu} in ③. For $b=2$, in the present problem

$$\phi_1 = c_{11}\chi_1 + c_{21}\chi_2$$

For real coefficients, the normalization condition is given by

$$\int |\phi_1|^2 d\tau = 1$$

The Fock matrix elements from ② with $b=2$ are given by

$$F_{11} = H_{11}^{core} + \frac{1}{2} P_{11} (11|11) + P_{12} (11|12) + P_{22} \left[(11|22) - \frac{1}{2} (12|21)\right]$$

($P_{12} = P_{21}$ for real functions)

$$F_{12} = F_{21} = H_{12}^{core} + \frac{1}{2} P_{11} (12|11) + P_{12} \left[\frac{3}{2} (12|12) - \frac{1}{2} (11|22)\right] + \frac{1}{2} P_{22} (12|22)$$

$$F_{22} = H_{22}^{core} + P_{11} \left[(22|11) - \frac{1}{2} (21|12)\right] + P_{12} (22|12) + \frac{1}{2} P_{22} (22|22).$$

So substituting the initial guess for P_{tu}'s and the values of H_{rs}^{core} and $(rs|tu)$ integrals, we will get the initial estimates of the F_{rs}'s.

The initial estimate of the secular eqn.

$$\det(F_{rs} - S_{rs} \varepsilon_i) = 0 \quad ④$$

is a 2×2 determinant, where the values of F_{rs} and S_{rs} are known. Solution of the two eqn.s, gives two values of orbital energy ε_i. Substitution of the lower root ε_1 into the Roothaan eqn ① with $r=2$ gives

$$C_{11}(F_{21} - \varepsilon_1 S_{21}) + C_{21}(F_{22} - \varepsilon_1 S_{22}) = 0$$

i.e. we get a new relation between C_{11} and C_{21} and finally, the improved coefficients C_{11} and C_{21}. Substitution of these improved coefficients C_{11} & C_{21} into ③ gives us the improved density matrix elements P_{tu}. Substitution of these improved P_{tu}'s into ② gives us the improved F_{rs} values and finally improved secular eqn. Solution of the improved secular eqn. gives improved orbital energy. Again solution of the Roothaan equation gives newly improved coefficients C_{11} and C_{21}. We have to repeat the cycle of calculation untill it gives converged-coefficients C_{11} and C_{21}.

The He ground-state SCF AO for the above basis set is

$$\phi_1 = C_{11}\chi_1 + C_{21}\chi_2$$

The SCF energy with $n=2$ and $b=2$ is

$$E_{HF} = \sum_{i=1}^{1} \varepsilon_i + \frac{1}{2}\sum_{r=1}^{2}\sum_{s=1}^{2} P_{rs} H_{rs}^{core}.$$