More accurately $v(r) = -\frac{Z}{r} + S(r)$ screening function

Such that $v(r) \to -\frac{Z}{r}$ as $r \to 0$

$$v(r) \to -\frac{1}{r} \quad \text{as } r \to \infty$$

Now let us think of N electrons

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla^2_{r_i} - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}}\right]\Psi(r_1, r_2 \ldots r_N)$$

$$= E\,\Psi(r_1, r_2 \ldots r_N)$$

Substituting $-\frac{Z}{r_i}$ by $V(r) - S(r)$ (Central) Screening function

$$H_{central} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla^2_{r_i} + V(r_i)\right)$$

Some effective central potential

$$H_1 = \left\{\sum_{i<j=1}^{N}\frac{1}{r_{ij}}\right\} - \sum_i S(r_i)$$

(Sph sum) → only the non central part of the int interaction term.

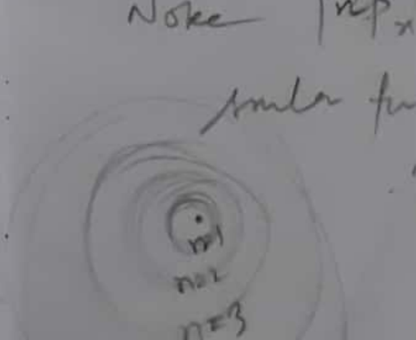
Contain a large sph sym part

H_1 can be small enough to be neglected or treated perturbatively.

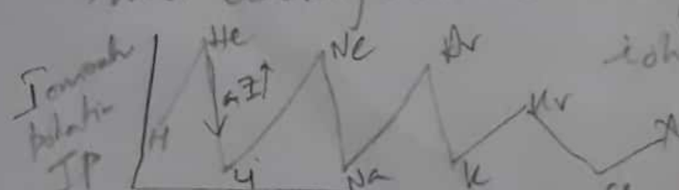
H_1 is negligible for ns electron since the $(n-1)$ shell is completely full and thus spherical in state

Note $|np_x|^2 + |np_y|^2 + |np_z|^2$ → spherical charge density

similar for all filled subshells.



∴ ns electron see spherical sym pot → most loosely bound → easy to ionize.



Now let us treat the interaction term exactly!

Note whether we use $V(r_i)$ or $\frac{Z}{r_i}$ the H_1 is completely separable in r_i and also the interaction term $\sum_{i<j=1}^{N} \frac{1}{r_{ij}}$ is insensitive to exchange of coordinates

$$\therefore \Phi(q_1 q_2 q_3 \cdots q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \cdots & \cdots & \cdots & \cdots \\ u_\alpha(q_N) & u_\beta(q_N) & \cdots & u_\nu(q_N) \end{vmatrix}$$

$q \to$ Space + Spin part
$\alpha \to n l s m_l m_s$
(Can also be $n l s j m_s$)

$$\left.\right\} u_{n l s m_l m_s}(q) = \psi_{n l m_l}(\vec{r}) \left[\chi\right]_{1\times 2}^{s m_s}$$

$$\Phi(q_1 q_2 \cdots q_N) = \frac{1}{\sqrt{N!}} \sum_{n=0}^{N!-1} (-1)^n P_n u_\alpha(q_1) u_\beta(q_2) \cdots u_\nu(q_N)$$

Ex:
$$\frac{1}{\sqrt{6}} \begin{vmatrix} u_1(1) & u_2(1) & u_3(1) \\ u_1(2) & u_2(2) & u_3(2) \\ u_1(3) & u_2(3) & u_3(3) \end{vmatrix} = \frac{1}{\sqrt{3!}} \big[u_1(1) u_2(2) u_3(3) - u_1(1) u_2(3) u_3(2) + u_2(1) u_3(2) u_1(3) - u_2(1) u_3(3) u_1(2) + u_3(1) u_1(2) u_2(3) - u_3(1) u_1(3) u_2(2) \big]$$

$P_{odd} \to$ odd # of Permutation
$P_{even} \to$ even # of Permutation

$$= \frac{1}{\sqrt{3!}} \Big[\underbrace{u_1(1) u_2(2) u_3(3)}_{\Phi_H} - \underline{P_{23}}\, \Phi_H + \underline{P_{13}}\, \underline{P_{23}}\, \Phi_H - \underline{P_{12}}\, \Phi_H + \underline{P_{13}}\, \underline{P_{12}}\, \Phi_H - \underline{P_{13}}\, \Phi_H \Big]$$

Note
$$\underbrace{P_{12} P_{23}}_{\text{Same}} \Phi_H = P_{12}\, u_1(1) u_2(3) u_3(2) = u_1(2) u_2(3) u_3(1)$$

$$\underline{P_{13} P_{12}} \Phi_H = P_{13}\, u_1(2) u_2(1) u_3(3) = u_1(2) u_2(3) u_3(1)$$

Check

Define $A = \frac{1}{N!}\sum_{n=0}^{N!-1}(-1)^n P_n \quad \therefore \quad \Phi = \sqrt{N!}\, A\, \Phi_H$

$\Rightarrow A^2 = A$

$E[\Phi] = \underbrace{\langle \Phi | H_1 | \Phi \rangle}_{\sum_i h_i} + \underbrace{\langle \Phi | H_2 | \Phi \rangle}_{\sum_{i<j=1}^{N} \frac{1}{r_{ij}}}$

$h_i = -\frac{\nabla^2_{r_i}}{2} - \frac{Z}{r_i}$

$\therefore [H, A] = 0, \quad [A, H_2] = 0$

$\langle \Phi | H_1 | \Phi \rangle = N! \langle \Phi_H | A H_1 A | \Phi_H \rangle$

$= N! \langle \Phi_H | H_1 A A | \Phi_H \rangle$

$= N! \langle \Phi_H | H_1 A | \Phi_H \rangle$

$= \sum_i \langle \Phi_H | h_i \sum_{n=0}^{N!-1} (-1)^n P_n | \Phi_H \rangle$ → only 1st term contributes since $\because \langle u_\alpha | u_\beta \rangle = \delta_{\alpha\beta}$

$= \sum_i \langle \Phi_H | h_i | \Phi_H \rangle$

$= \sum_\lambda \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle$

$= \sum_\lambda I_\lambda$

$\langle \Phi | H_2 | \Phi \rangle = N! \langle \Phi_H | A H_2 A | \Phi_H \rangle$

$= N! \langle \Phi_H | H_2 A^2 | \Phi_H \rangle$

$= N! \langle \Phi_H | H_2 A | \Phi_H \rangle$

$= \sum_{i<j=1}^{N} \langle \Phi_H | \frac{1}{r_{ij}} \sum_{n=0}^{N!-1} (-1)^n P_n | \Phi_H \rangle$

1st term ↙ ↙ only one more term

$= \sum_{i<j} \left[\langle \Phi_H | \frac{1}{r_{ij}} | \Phi_H \rangle - \langle \Phi_H | \frac{1}{r_{ij}} P_{ij} | \Phi_H \rangle \right]$

$= \sum_{\text{all pairs}} \left[\langle u_\lambda(q_i)\, u_\mu(q_j) | \frac{1}{r_{ij}} | \cdots \rangle - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_j) u_\mu(q_i) \rangle \right]$

$$= \frac{1}{2}\sum_{i}^{N}\sum_{j}^{N}\left[J_{\lambda\mu} - K_{\lambda\mu}\right]$$

$$J_{\lambda\mu} = \left\langle u_\lambda(q_i)\, u_\mu(q_j) \right| \frac{1}{r_{ij}} \left| u_\lambda(q_i)\, u_\mu(q_j) \right\rangle$$
→ Direct term

$$K_{\lambda\mu} = \left\langle u_\lambda(q_i)\, u_\mu(q_j) \right| \frac{1}{r_{ij}} \left| u_\lambda(q_j)\, u_\mu(q_i) \right\rangle$$
→ Exchange term

$$E[\Phi] = \sum_\lambda \left[I_\lambda + \frac{1}{2}\sum_\mu \left(J_{\lambda\mu} - K_{\lambda\mu}\right)\right]$$

Now we will variationally minimise $E[\Phi]$ with respect to variation in the spin orbitals $\{u_\alpha u_\beta \dots u_N\}$ subject to N^2 orthonormality requirements $\langle u_\mu | u_\lambda\rangle = \delta_{\mu\lambda}$

∴ The variational equation reads as:

$$\delta E[\Phi] - \sum_\lambda \sum_\mu \varepsilon_{\lambda\mu}\, \delta\langle u_\mu | u_\lambda\rangle = 0 \quad (A)$$

∴ Now $E^*[\Phi] = E[\Phi]$ ∴ $\delta E^*[\Phi] - \sum_\lambda\sum_\mu \varepsilon^*_{\lambda\mu}\, \delta\langle u_\lambda | u_\mu\rangle = 0$

However as per (A) → $\delta E[\Phi] - \sum_\lambda\sum_\mu \varepsilon_{\mu\lambda}\, \delta\langle u_\lambda | u_\mu\rangle = 0 \Rightarrow \varepsilon^*_{\lambda\mu} = \varepsilon_{\mu\lambda}$

∴ ε is Hermitian

Then we can consider $\{u_\lambda\}$ which are yet to be found, to be already constituting the eigen subspace of ε, and we seek to variationally minimise $E[\Phi]$ in such a subspace. We are allowed to do so since $E[\Phi]$ remains unaltered in such a $\{u_\lambda'\}$ basis, due to the unitarity of the transformation for $\{u_\lambda\}$ to $\{u_\lambda'\}$

$$\left[h_i \right] u_\lambda(q_i) + \left[\sum_\mu \int u^*_\mu(q_j) \frac{1}{r_{ij}} u_\mu(q_j)\, dq_j \right] u_\lambda(q_i)$$

$$- \sum_\mu \left[\int u^*_\mu(q_j) \frac{1}{r_{ij}} u_\lambda(q_j)\, dq_j \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i)$$

$\longrightarrow$ HF Eqn

$u_\lambda(q_i) = u_\lambda(r_i)\, \chi_{\frac{1}{2} m_s^\lambda}$

In term of only the spatial part

Intigro-differential Eqn:

$$\left[h_i \right] u_\lambda(\vec{r}_i) + \left[\sum_\mu \underbrace{\int |u_\mu(r_j)|^2 \frac{1}{r_{ij}} dr_j}_{V_\mu^d(r_i)} \right] u_\lambda(r_i)$$

$$- \sum_\mu \underbrace{\delta_{m_s^\lambda m_s^\mu}}_{\text{from spin part}} \left[\underbrace{\int u^*_\mu(r_j) \frac{1}{r_{ij}} u_\lambda(r_j)\, dr_j}_{f(r_i)} \right] u_\mu(r_i) = E_\lambda u_\lambda(r_i)$$

$$V_\mu^d(r_i) = \int \frac{|u_\mu(r_j)|^2}{r_{ij}} dr_j \quad \left[= V_\mu^d(q_j) \text{ since spin part integrate to } 1 \right.$$

$$\therefore \sum_\mu V_\mu^d(r_i) = \int \sum_\mu \frac{|u_\mu(r_j)|^2}{r_{ij}} dr_j = \int \frac{\varphi(r_j)}{r_{ij}} dr_j$$

$$\underbrace{V_\mu^{ex}(q_i) u_\lambda(q_i)} = \left[\int u^*_\mu(q_j) \frac{1}{r_{ij}} u_\lambda(q_j)\, dq_j \right] u_\mu(q_i)$$

$$= \delta_{m_s^\lambda m_s^\mu} \left[\int u^*_\mu(r_j) \frac{1}{r_{ij}} u_\lambda(r_j)\, dr_j \right] u_\mu(r_i) \cdot \left[\chi_{\frac{1}{2} m_s^\mu} \right]$$

$$= \delta_{m_s^\lambda m_s^\mu} \underbrace{V_\mu^{ex}(r_i) u_\lambda(r_i)} \left[\chi_{s\, m_s^\mu} \right]$$

$$\Rightarrow \left[h_i + \sum_\mu V_\mu^d(r_i) - \sum_\mu V_\mu^{ex}(q_i) \right] u_\lambda(q_i) = E_\lambda u_\lambda(q_i)$$

Note that this looks simple but not actually a Eigen Value Eqn

Note that

$$v^{ext}_{\lambda}(q_i)\, u_{\lambda}(q_i) = \left[\int u^*_{\lambda}(q_j)\frac{1}{r_{ij}} u_{\lambda}(q_j)\, dq_j\right] u_{\lambda}(q_i)$$

$$= \left[\int \frac{|u_{\lambda}(q_j)|^2}{r_{ij}}\, dq_j\right] u_{\lambda}(q_i)$$

$$= v^d_{\lambda}(q_i)\, u_{\lambda}(q_i)$$

$\Rightarrow$ No self energy correction; μth orbital doesn't effect it self. It is effected only by other orbitals

$\therefore$ Say for $\lambda = 1$ with $N = 2$

$$\left[h + v^d_2(r) - v^{ex}_2(r)\right] u_1(r) = E_1 u_1(r)$$

$$\Rightarrow \left[h + \int \frac{|u_2(r')|^2}{|r-r'|} dr'\right] u_1(r) - \int u_2(r')\frac{1}{|r-r'|} u_1(r')\, dr'\, u_2(r) = E_1 u_1(r)$$

Now let $u_1(r) = \sum_m c_{1m}\phi_m(r)$; $\{\phi\} \to$ basis set

$u_2(r) = \sum_p c_{2p}\phi_p(r)$

$$\therefore \langle \phi_l(r)| \left[\quad \cdots \quad = \quad \cdots \right]$$

$$\Rightarrow \sum_m c_{1m}\langle l|h|m\rangle + \sum_m\sum_p\sum_q c^*_{2p}c_{2q} \underbrace{\langle l| \left[\int \frac{\phi^*_p(r')\phi_q(r')\, dr'}{|r-r'|}\right]|m\rangle}_{D_{lpqm}} c_{1m}$$

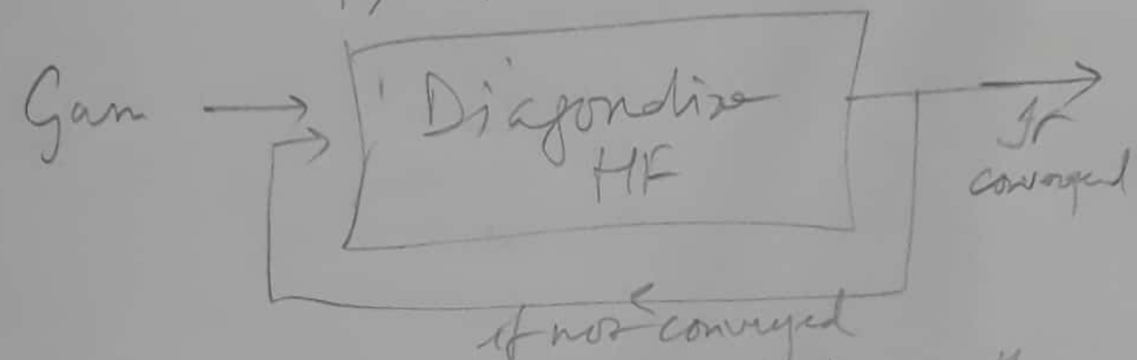
$$- \sum_m\sum_p\sum_q c^*_{2p}c_{1m} \underbrace{\langle l|\left[\int \frac{\phi^*_p(r')\phi_m(r')\, dr'}{|r-r'|}\right]|p\rangle}_{X_{lpqm}} c_{2p} = \sum_n E_1 c_{1n}\langle l|n\rangle$$

$$\Rightarrow \sum_m c_{1m}[HF]_{lm} = E_1 \sum_n c_{1n} S_{ln}$$ $\to$ Generalised Eigen Value Eq.

Solve for $\{c_{1i}\}$ and $\{c_{2i}\}$ self consistently from starting with a guess

Given $\{c_{1i}\}$, $\{c_{2i}\}$. Evaluate D and X.

[For a CONS basis $\langle l|m\rangle = \delta_{lm} \Rightarrow \sum_m [HF]_{lm} C^T_{m1} = E_1 C^T_{l1}$]



Convergence: If the difference between the present set of $\{c_{1i}\}$ and $\{c_{2i}\}$ differ from those of the previous iteration less than a very small number.

Total energy:

Recall, $E[\Phi] = \sum_\lambda \left[I_\lambda + \frac{1}{2} \sum_\mu (J_{\lambda\mu} - K_{\lambda\mu}) \right]$

$\langle u_\lambda(q_i)|$ [HF eqn]:

$$I_\lambda + \sum_\mu [J_{\lambda\mu} - K_{\lambda\mu}] = E_\lambda$$

$$\therefore \sum_\lambda E_\lambda = \sum_\lambda I_\lambda + \sum_\lambda \sum_\mu [J_{\lambda\mu} - K_{\lambda\mu}]$$

$$\therefore E[\Phi] = \sum_\lambda E_\lambda - \frac{1}{2} \sum_\lambda \sum_\mu [J_{\lambda\mu} - K_{\lambda\mu}] = E_N$$

$$= \sum_\lambda I_\lambda + \frac{1}{2} \sum_\lambda \sum_\mu [J_{\lambda\mu} - K_{\lambda\mu}]$$

$\therefore$ Ionization energy $\Delta = E_N - E_{N-1} = I_N + \frac{1}{2} \left[J_{NN} - K_{NN} + \sum_\mu (J_{N\mu} - K_{N\mu}) + \sum_\lambda (J_{\lambda N} - K_{\lambda N}) \right]$

$\Rightarrow \boxed{\Delta = I_N + \sum_\lambda J_{\lambda N} - K_{\lambda N} = E_N}$ Koopmans' theorem