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Seminar on Chemical Bond

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$N \gg 1$ atoms, placed at $\overrightarrow{R}_i$, $i = 1, 2, ..., N$, Hartree-Fock (HF) eqs, one-electron orbitals s

1 Molecular orbitals

$$\Downarrow$$

$$\boxed{\Psi_s = \alpha_s \varphi_s + \beta_s \Phi_s}$$

$$\varphi_s = \sum_{i,a} c^s_{ia} \chi_{ia}(\overrightarrow{r}) = \sum_{i,a} c^s_{ia} \chi_a(\overrightarrow{r} - \overrightarrow{R}_i)$$

2 Minimization of the HF energy functional

$$\Downarrow$$

1. $\beta_s \neq 0$ for valence orbitals (fractional occupancy)
2. $E = E_a(\varphi_s) - \Delta E + E_b(\phi_s)$
3. $E_b(\phi_s) \Rightarrow$ eff. hamiltonian H_b
4. H_b : electrons in a background of ionic cores

$$\rho(\overrightarrow{r}) == \sum_{ia;jb} \left(\sum_s \beta^2_s c^{s*}_{ia} c^s_{jb} \right) \chi^*_{ia}(\overrightarrow{r}) \chi_{jb}(\overrightarrow{r})$$

$$\Downarrow$$

$$H_b = \sum_\alpha \frac{p^2_\alpha}{2m} - e^2 \int d\overrightarrow{r} d\overrightarrow{r}' \frac{\rho(\overrightarrow{r})}{|\overrightarrow{r} - \overrightarrow{r}'|} n(\overrightarrow{r}') +$$

$$+\frac{e^2}{2}\int d\overrightarrow{r}d\overrightarrow{r}'\frac{n(\overrightarrow{r})n(\overrightarrow{r}')}{|\overrightarrow{r}-\overrightarrow{r}'|}-\frac{e^2}{2}\int d\overrightarrow{r}d\overrightarrow{r}'\frac{n(\overrightarrow{r},\overrightarrow{r}')n(\overrightarrow{r}',\overrightarrow{r})}{|\overrightarrow{r}-\overrightarrow{r}'|}+$$

$$+\frac{e^2}{2}\int d\overrightarrow{r}d\overrightarrow{r}'\frac{\rho(\overrightarrow{r})\rho(\overrightarrow{r}')}{|\overrightarrow{r}-\overrightarrow{r}'|}$$

$$n(\overrightarrow{r})=\sum_s|\Phi_s(\overrightarrow{r})|^2$$

$$n(\overrightarrow{r},\overrightarrow{r}')=\sum_s\Phi_s^*(\overrightarrow{r})\Phi_s(\overrightarrow{r}')$$

$$\varphi(\overrightarrow{r})=e\int d\overrightarrow{r}'\frac{\rho(\overrightarrow{r}')}{|\overrightarrow{r}-\overrightarrow{r}'|}-e\int d\overrightarrow{r}'\frac{n(\overrightarrow{r}')}{|\overrightarrow{r}-\overrightarrow{r}'|}$$

$$\Downarrow$$

5. Main contribution from H_b, for occupancy $\beta_s=1$, through
quasi-classical description
H_b: Quasi-classical H_b + quantum corrections
$E_\alpha(\varphi_s)-\Delta E$: independent atoms + quantum corrections
Delocalization (spatial extension)
Binding energy
Small quantum corrections, of opposite signs, short-scale length (fractional occupancy included)

3 Quasi-classical description for H_b

1. Large $N\gg 1$ $\Rightarrow$ slow variations $\Rightarrow$ plane waves for the HF eqs

$$\boxed{n=k_F^3/3\pi^2}$$

2. $E_b=\underbrace{T(n)+U_{e-i}(n)+U_{e-e}(n)}+ + E_{ex}+E_{i-i}$
3. Density functional; δn, slightly-inhomogeneous electron liquid

$$\Downarrow$$

$$\boxed{\frac{\hbar^2}{2m}k_F^2-e\varphi=0}$$

Self-consistent Hartree field φ

$$\boxed{\Delta\varphi=-4\pi e\rho+4\pi en}$$

4. Thomas-Fermi theory
5. Linearization

4 Linearization

$$k_F^2 \;\rightarrow\; \overline{k}_F \cdot k_F$$

$$\uparrow$$

variational

$$\frac{1}{2}\overline{k}_F \cdot k_F - \varphi = 0 \;\Rightarrow\; k_F = 2\varphi/\overline{k}_F$$

$$n = \frac{1}{3\pi^2}\overline{k}_F^2 k_F = \frac{2}{3\pi^2}\overline{k}_F \cdot \varphi = \frac{q^2}{4\pi}\varphi$$

$q^2 = \frac{8}{3\pi}\overline{k}_F$		$k_F = \frac{16}{3\pi q^2}\varphi$

$$\Delta\varphi = -4\pi\rho + q^2\varphi$$

$$k_{F_{av}} = \frac{1}{N}\int d\overrightarrow{r}\, n k_F =$$

$$= \frac{1}{N}\frac{4}{3\pi^2}\int d\overrightarrow{r}\,\varphi^2 \sim \frac{3\pi}{8}q^2 = \overline{k}_F$$

$$q_{var}^2 \sim \frac{1}{N}\frac{32}{9\pi^3}\int d\overrightarrow{r}\,\varphi^2 = q_{av}^2$$

Quantum corrections, short-scale length
Kinetic energy

$$T = \frac{V}{10\pi^2}k_F^5 \;\rightarrow\; \frac{\overline{k}_F^4}{10\pi^2}\int d\overrightarrow{r}\, k_F == \frac{\pi}{5}(3/8)^3 q^6 \int d\overrightarrow{r}\,\varphi$$

Potential energy

$$E_{pot} = -\int d\overrightarrow{r}(\varphi n - \frac{1}{2}\varphi_e n) + E_{i-i}$$

$$= -\frac{1}{2}\int d\overrightarrow{r}(\varphi + \varphi_i)n + E_{i-i} = -\frac{q^2}{8\pi}\int d\overrightarrow{r}(\varphi + \varphi_i)\varphi + E_{i-i}$$

$$\varphi_i = \int d\overrightarrow{r}\,' \frac{\rho(\overrightarrow{r}\,')}{|\overrightarrow{r} - \overrightarrow{r'}|}$$

$$E_{i-i} = \frac{1}{2}\int d\overrightarrow{r}\,\varphi_i \rho$$

Quasi-classical energy

$$E_q = T + E_{pot} \qquad (q)$$

$$\Downarrow \text{Minimization}$$

$$\boxed{q,\ E_q,\ \overrightarrow{R}_i}$$

Exchange energy

$$E_{ex} = -\frac{Vk_F^4}{4\pi^3} \ \rightarrow \ -\frac{\overline{k}_F^3}{4\pi^3}\int d\overrightarrow{r}k_F = \frac{4}{3\pi}(3/8)^3 q^4 \int d\overrightarrow{r}\varphi$$

Binding energy

$$E = E_q + E_{ex}$$

Quantum corrections

$$-\frac{\hbar^2}{2m}\Delta\psi - e\varphi\psi = \varepsilon\psi$$

$$\Downarrow$$

Electronic properties (Fermi level, spectrum, LUMO, HOMO, etc)
Ionization potential

$$I = (1-\beta^2)I_{at} + \underbrace{\beta^2 I_{el}}$$

$$\sim 0$$

5 Point-like ionic cores; Metallic clusters

$$\rho(\overrightarrow{r}) = \sum_{ia;jb}\left(\sum_s \beta_s^2 c_{ia}^{s*}c_{jb}^s\right)\chi_{ia}^*(\overrightarrow{r})\chi_{jb}(\overrightarrow{r}) \cong \beta^2\sum_{ia}|\chi_{ia}|^2$$

$$\Downarrow$$

$$\boxed{\beta^2 z_i = z_i^*}$$

$$\uparrow \qquad \uparrow$$

valence effective valence

$$\boxed{\rho(\overrightarrow{r}) = \textstyle\sum_i z_i^*\delta(\overrightarrow{r} - \overrightarrow{R}_i)}$$

$$\begin{cases} H_b = \sum_\alpha p_\alpha^2/2m - e^2\sum_{i\alpha}\frac{z_i^*}{|\overrightarrow{R}_i - \overrightarrow{r}_\alpha|} + \\ \\ +\frac{1}{2}e^2\sum_{\alpha\beta}\frac{1}{|\overrightarrow{r}_\alpha - \overrightarrow{r}_\beta|} + \frac{1}{2}e^2\sum_{ij}\frac{z_i^* z_j^*}{|\overrightarrow{R}_i - \overrightarrow{R}_j|} \\ \\ \varphi = e\sum_i \frac{z_i^*}{|\overrightarrow{R}_i - \overrightarrow{r}|} - e\int d\overrightarrow{r}\,\frac{n(\overrightarrow{r}')}{|\overrightarrow{r} - \overrightarrow{r}'|} \end{cases}$$

$$\boxed{n = \frac{q^2}{4\pi e}\varphi}$$

$$\begin{cases} \Delta\varphi = -4\pi \sum_i z_i^* \delta(\overrightarrow{r} - \overrightarrow{R}_i) + q^2\varphi \\ \varphi = \sum_i \frac{z_i^*}{|\overrightarrow{r} - \overrightarrow{R}_i|} \exp\left\{-q|\overrightarrow{r} - \overrightarrow{R}_i|\right\} \end{cases}$$

Kinetic energy:

$$T = \frac{27\pi^2}{640} z_0 q^4 = Aq^4/4 \ , \ z_0 = \sum_i z_i^*$$

Potential energy:

$$\boxed{\begin{array}{c} E_{pot} = -\frac{q}{4}\left[3\sum_i z_i^{*2} + \right. \\ \left. + \sum_{i\neq j} z_i^* z_j^* \left(1 - \frac{2}{q|\overrightarrow{R}_i - \overrightarrow{R}_j|}\right) e^{-q|\overrightarrow{R}_i - \overrightarrow{R}_j|}\right] \\ = -Bq \end{array}}$$

"self-energy" interaction

Inter-atomic potentials

$$\boxed{\phi_{ij} = -\frac{1}{2} q z_i^* z_j^* \left(1 - \frac{2}{qR_{ij}}\right) e^{-qR_{ij}}}$$

$$\overrightarrow{X}_i = q\overrightarrow{R}_i \ , \ R_{ij} \sim X_{ij}/q \sim c/q = a$$

$$\boxed{c \cong 2.73}$$

inter-atomic distance a

Quasi-classical energy

$$E_q = Aq^4/4 - Bq = -\frac{3}{4}Bq$$

$$\Downarrow$$

$$\boxed{q = (B/A)^{1/3} \cong 0.77 \cdot z^{*1/3}}$$

$$\boxed{E_q \cong -0.43 \cdot N \cdot z^{*7/3}}$$

Exchange energy

$$E_{ex} = -(9/32)q^2 N z^* \cong -0.17 \cdot N \cdot z^{*5/3}$$

$$\boxed{E = -0.43 \cdot N \cdot z^{*7/3} - 0.17 \cdot N \cdot z^{*5/3}}$$

$$a \cong c/q \sim 3.5/z^{*1/3}$$

Quantum corrections

$$q_{av} \cong 0.9 z^{*1/3} \sim 0.77 z^{*1/3} = q_{var}$$

$$\Downarrow$$

17%

6 Atoms and effective valence

$\varphi = Ze^{-qr}/r$, $E_q = -11.78 \cdot Z^{7/3}$ eV ($E_{ex} = -4.6 \cdot Z^{5/3}$ eV)

$\Delta E = -4.56 \cdot Z^{7/3}$ eV

$E = -16.34 \cdot Z^{7/3}$ eV $\sim E_{emp} = -16 \cdot Z^{7/3}$ eV

$$\left.\begin{array}{c} q = 0.77 \cdot Z^{1/3} \\ q_{av} = 0.9 \cdot Z^{1/3} \end{array}\right\} \overline{q} = 0.84 \cdot Z^{1/3}$$

$$N_{out} = \int_{r>R} d\overrightarrow{r} \cdot n =$$

$$= q^2 \int_R^\infty dr \cdot r^2 \varphi = Z(1+qR)e^{-qR}$$

$$\boxed{z^* = \tfrac{N_{out}}{Z} \cdot z = z(1+qR)e^{-qR}}$$

$$\beta^2 = N_{out}/Z$$

$$\boxed{z^* = z(1+0.84Z^{1/3})e^{-0.84Z^{1/3}}}$$

$(R = 1)$

	Z	z	z^*	β^2
Na	11	1	0.44	0.44
K	19	1	0.34	0.34
Fe	26	2	0.57	0.28
Ag	47	1	0.19	0.19
Ba	56	2	0.34	0.17

7 Magic numbers

N= 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61

$$D = \ln\left(I_N^2/I_{N-1}I_{N+1}\right) = E_{N+1} + E_{N-1} - 2E_N$$

Stability- vibrational spectra (10^{-4} eV/A)
Isomers
Statistical magic numbers
Electronic magic numbers (2, 8, 20, ...)

$$\varphi = \overline{\sum_i \frac{z_i^*}{|\overrightarrow{r} - \overrightarrow{R}_i|} e^{-q|\overrightarrow{r} - \overrightarrow{R}_i|}} =$$

$$= const. - Ax^2 - By^2 - Cz^2 : ...$$

(Clemenger-Nilson potential)

$const. \sim (4\pi/c^3)z^*q \sim (4\pi/c^2)\frac{z^*}{a}$

8 Polarizability

$$-\frac{4\pi}{q^2}n\delta n - \frac{1}{2}\varphi_i \delta n + \overrightarrow{E}\,\overrightarrow{r}\cdot n = 0$$

(pot. energy)

$$\delta n = \frac{q^2}{4\pi}\frac{\varphi}{\varphi+\varphi_i/2}\overrightarrow{E}\,\overrightarrow{r}$$

$$\delta E = -\frac{q^2}{4\pi}\int d\overrightarrow{r}\left(\frac{\varphi}{\varphi+\varphi_i/2}\right)^2\left(\overrightarrow{E}\,\overrightarrow{r}\right)^2$$

$\chi_e \sim \frac{32}{15c^2}\cdot a^2 R$, R - cluster radius

$(c \cong 2.73)$

9 Diamagnetic susceptibility

$$\delta E = -\frac{e^2}{8mc^2}\sum_\alpha \overline{\left(\overrightarrow{H}\times \overrightarrow{r}_\alpha\right)^2} =$$

$$= -\frac{e^2H^2}{12mc^2}\sum_\alpha \overline{r_\alpha^2} = -\frac{e^2H^2}{12mc^2}\int d\overrightarrow{r}\cdot r^2 n$$

$$\Downarrow$$

$$\chi_d \sim -0.54\cdot 10^{-4}\,(2\pi/15)\left(z^* R^5/a^3\right)\cdot a_H$$

10 Plasmons

$$T(n) + U_{e-i}(n) + U_{e-e}(n)$$

$\delta n = -n\cdot div\,\overrightarrow{n}$
$\delta^{(1)} = 0$

$$\delta^{(2)} \Rightarrow \begin{cases} T = \frac{1}{2}\int d\overrightarrow{r}\cdot nm\,\dot{\overrightarrow{u}}^2 \\ U = \frac{1}{2}\int d\overrightarrow{r}\,d\overrightarrow{r}'\frac{e^2}{|\overrightarrow{r}-\overrightarrow{r}'|}\cdot \\ \quad\cdot\delta n(\overrightarrow{r})\delta n(\overrightarrow{r}') \end{cases}$$

$$\omega = \left(\frac{4\pi n^2 e^2}{nm}\right)^{1/2}$$

$$\Big\Downarrow n\to\beta^2 n$$

$$\boxed{\omega = \beta\,(4\pi n e^2/m)^{1/2}}$$

(fractional occupancy)

11 Quasi-classical quasi-particles

$$f(\overrightarrow{k} - \overrightarrow{k'}) = 4\pi e^2 \sum_i \frac{z_i^*}{q^2 + |\overrightarrow{k} - \overrightarrow{k'}|^2} e^{i(\overrightarrow{k}-\overrightarrow{k'})\overrightarrow{R}_i}$$

$$f(\overrightarrow{p} - \overrightarrow{p'}) = f \cdot \frac{(2\pi\hbar)^3}{V}\delta(\overrightarrow{p} - \overrightarrow{p'})$$

$$f = 4\pi N e^2 z^*/q^2$$

$$\delta n_{\overrightarrow{p}} = -\delta(\varepsilon - \varepsilon_F)\cdot\delta\varepsilon$$

$$\downarrow$$

$$1/\Delta\varepsilon,\ \Delta\varepsilon = (p_F/m)(\pi\hbar/a)$$

$$\varepsilon_F = \frac{1}{2}\overline{k}_F k_F = (3\pi/16)q^2 k_F = (4\pi/c^3)z^* q \quad (= \overline{\varphi})$$

$$\boxed{m^* = m\cdot\left(1 + 0.39 z^{*1/3}\right)}$$

$$C = V\rho^*\pi^2 T/3\ ,\ \rho^* = p_F m^*/\pi^2\hbar^3$$

- no electronic compressibility (adiabatic)
- no electronic sound, zero-sound (immersed into el-hole excs.)
-lifetime

$$\gamma = \frac{1}{\tau} = \frac{\pi}{2\hbar}\left(\frac{4\pi e^2 N z^*}{V q^2}\right)^2 \left(\frac{\rho}{n}\right)^3 \frac{(\Delta\varepsilon)^2 + \pi^2 T^2}{e^{\mp(\varepsilon-\varepsilon_F)/T} + 1}$$

-no renormalized Pauli spin paramagnetic susceptibility
($\chi = \frac{1}{4}g^2\mu_B^2\rho$, $\mu_B = e\hbar/2mc$: $\mu_B H \simeq 0.67K$, $H = 1T = 10^4 Gs$)

12 Ionization potentials

$$I = (1-\beta^2)I_a$$

	I_{th} (eV)	I_{exp} (eV)
Na	2.88	3.5
K	2.86	2.8
Fe	5.67	
Ag	6.13	5.5
Ba	4.32	

13 Magnetic momentum of cluster-Fe by Hund's rule

$$Fe - 3d^6 \quad \begin{matrix}\uparrow\\ \uparrow\\ \uparrow\\ \uparrow\\ \uparrow\downarrow\end{matrix} \quad = 4\mu_B$$

0.57 go to the chem. bond

$$6 - 0.57 = 5.43 : left \quad \begin{matrix}\uparrow\\ \uparrow\\ \uparrow\\ \uparrow\\ \uparrow{:}\downarrow\ 0.43\end{matrix} \quad \Rightarrow 4 + 0.57 = 4.57\mu_B$$