I. State the original Hohenberg–Kohn Theorem-1 (HKT-1) and prove it by the approach of contradiction.

HKT-1 Proof: The Statement is that $\rho(r)$ determines $v(r)$.
i.e $v(r)$ is a unique functional of $\rho(r)$

The Hamiltonian for a many electron System under external potential $v(r)$ $\left[\hat{V} = \sum_i v(r_i)\right]$ can be written as

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}$$

Let E_0 be the ground state energy of the above $\hat{H}$ under the defined external potential $\hat{V}$.

i.e $\quad E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$

the ground State electron density for $\hat{V}$ can be also written as

$$\rho_0(r) = \int |\Psi_0|^2 d^3r$$

for a $\hat{V}$, we have have ground state $\rho_0(r)$, E_0, and Ψ_0

Now Let's assume that for a $\hat{V}'$, we have the same $\rho_0(r)$ but a different E_0' and Ψ_0'.

i.e $\quad \rho_0'(r) = \int |\Psi_0'|^2 d^3r = \rho_0(r)$

$$\rho_0'(r) = \rho_0(r)$$

According to variational principle

$$E_0' < \langle \psi_0 | \hat{H}' | \psi_0 \rangle = \langle \psi_0 | \hat{H} + \hat{V}' - \hat{V} | \psi_0 \rangle$$

$$= \underbrace{\langle \psi_0 | \hat{H} | \psi_0 \rangle} + \langle \psi_0 | \hat{V}' - \hat{V} | \psi_0 \rangle$$

$$= E_0 + \int \rho_0(r) [\hat{V}' - \hat{V}] d^3r$$

$$\therefore \boxed{E_0' < E_0 + \int \rho_0(r) [\hat{V}' - \hat{V}] d^3r} \quad \text{— ①}$$

Now consider

$$E_0 < \langle \psi_0' | \hat{H} | \psi_0' \rangle = \langle \psi_0' | \hat{H}' + \hat{V} - \hat{V}' | \psi_0' \rangle$$

$$= \underbrace{\langle \psi_0' | \hat{H}' | \psi_0 \rangle} + \langle \psi_0' | \hat{V} - \hat{V}' | \psi_0' \rangle$$

$$= E_0' + \int \rho_0'(r) [\hat{V} - \hat{V}'] d^3r$$

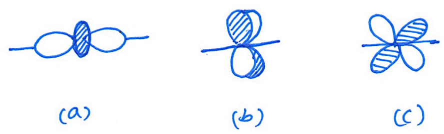
$$\therefore E_0 < E_0' + \int \rho_0'(r) [\hat{V} - \hat{V}'] d^3r$$

$$\because \rho_0'(r) = \rho_0(r)$$

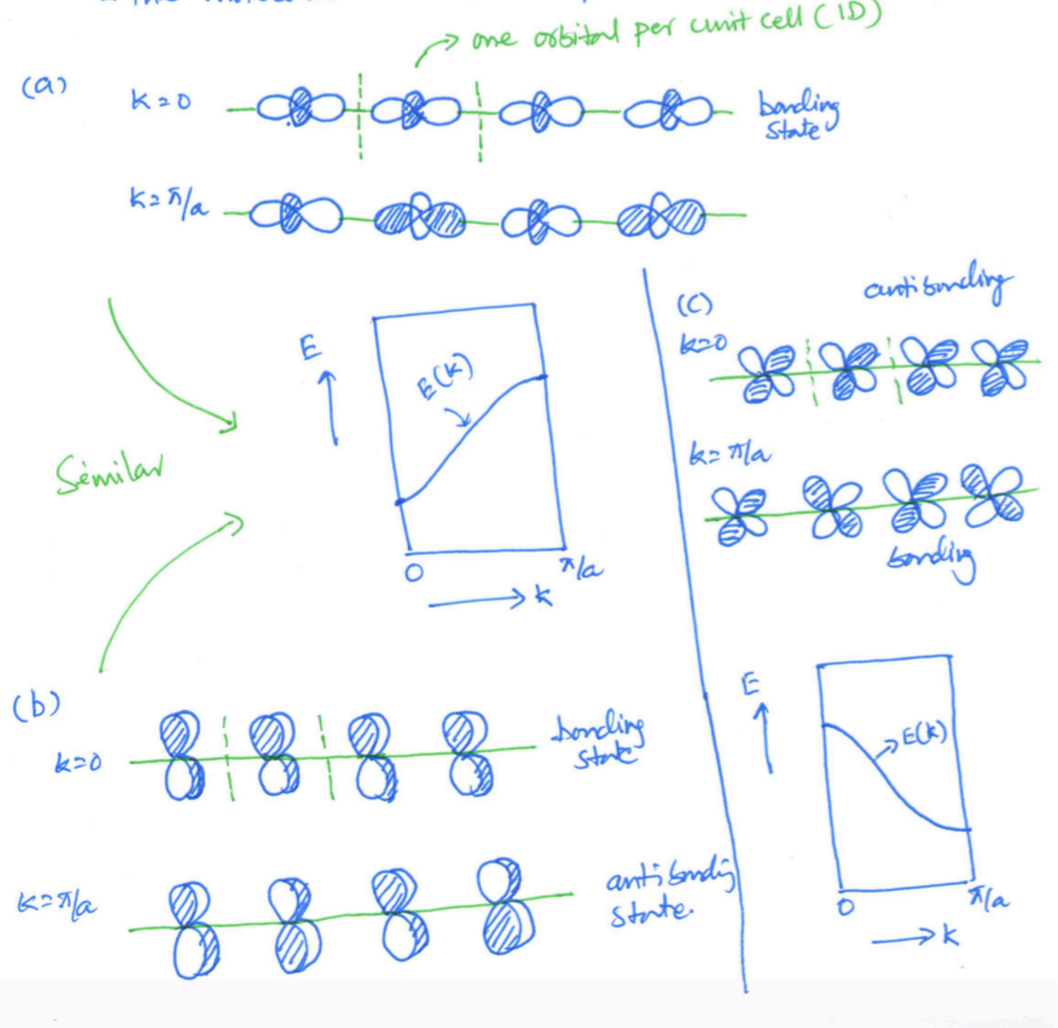
$$\therefore \boxed{E_0 < E_0' + \int \rho_0(r) [\hat{V} - \hat{V}'] d^3r} \quad \text{— ②}$$

Eqn ① & ② contradict to each other. Therefore $V(r)$ is a unique functional of $\rho(r)$.

II. Using the orbitals given below sketch schematic electronic band dispersion diagrams for each separately and depict the possible graphic solutions of the crystal orbitals for four unit cells at $k = 0$ and π/a. Consider an orbital per unit cell.



We encounter these metal d-orbitals when Fe(111) interacts with the N_2 molecule – vice-versa – the molecular reactions on surfaces....



III. Determine d_{111} in tetragonal unit cell, a = 3.2 Å and c = 4.2 Å.

For tetragonal unit cell the interplanar spacing d_{hkl}

$$\frac{1}{d_{hkl}^2} = \left[\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}\right] \Rightarrow d_{hkl} = \left[\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}\right]^{-1/2}$$

$$\therefore \quad d_{111} = \left[\frac{1+1}{10.24} + \frac{1}{17.64}\right]^{-1/2} = \left[0.195 + 0.057\right]^{-1/2}$$

$$= \left[0.252\right]^{-1/2}$$

$$\therefore \boxed{d_{111} = 1.99 \approx 2.0}$$

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