/2018

Lec. 17

Homogeneous (Free) Electron Gas – Jellium

~~We saw that the in the Jellium model for a metal with free electrons we~~ "A system of electrons moving under no external forces is called a free-electron gas", even though electrons are interacting w/ each other." — Raimes.

We assume (Jellium) that the electrons move in a uniform positive background ~~densi~~ charge density equal in magnitude to the electronic charge density: $-n = -N/V$.

Let's assume N electrons in a cubic box (w/ PBC) of volume $V = L^3$: Given the translational symmetry it can be shown that the HF eigenfunctions of this system are the functions:

$$\left.\begin{aligned} \psi_{\vec{k}\tau}(x) &= \varphi_{\vec{k}}(\vec{r})\,\chi_{\tau}(\sigma) \\ \text{w/}\quad \vec{k} &= \frac{2\pi}{L}(l_1, l_2, l_3) \end{aligned}\right\} \text{ where } l_i \in I \qquad \text{— (329)}$$

The wavevectors of the occupied ~~subspace of~~ orbitals in the HF Slater determinant lie w/in a sphere in reciprocal space of radius k_F (fermi wavevector). Each $\vec{k}$ state is doubly occupied by e's w/ opposite spin.

The RHF eq'ns of the system are:

$$\Bigg\{ -\frac{\nabla^2}{2} - \underbrace{\int \frac{n\, d^3r'}{|\vec{r}-\vec{r}'|}}_{\substack{\text{attraction}\\ \text{of Jellium}\\ \text{background}}} + \underbrace{\int d^3r' \frac{2\sum_{k'\leq k_F} |\varphi_{\vec{k}'}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}}_{\text{Hartree potential}} - \overbrace{\sum_{k'\leq k_F} \int d^3r' \frac{\varphi^*_{\vec{k}}(\vec{r}')\,\hat{P}_{12}\,\varphi_{\vec{k}'}(\vec{r}')}{|\vec{r}-\vec{r}'|}}^{\text{exchange}} \Bigg\}$$

$$\times\, \varphi_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k})\,\varphi_{\vec{k}}(\vec{r}) \qquad \text{— (330)}$$

$$\therefore \quad 2\sum_{\vec{k}'<k_F} |\varphi_{k'}(\vec{r})|^2 = 2\sum_{\vec{k}<k_F} \frac{1}{V} = n \quad \text{—} \ (331)$$

the Hartree potential exactly cancels the background term

We get

$$\left[-\frac{\nabla^2}{2} + v_x(\vec{r})\right]\varphi_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k})\,\varphi_{\vec{k}}(\vec{r}) \quad \text{—} \ (332)$$

$$v_x(\vec{r})\varphi_{\vec{k}}(\vec{r}) = \sum_{k'<k_F} \frac{1}{V}\int d^3r' \, \frac{e^{-i\vec{k}'\cdot\vec{r}'}\, e^{i\vec{k}\cdot\vec{r}'}}{|\vec{r}-\vec{r}'|} \times \frac{e^{i\vec{k}'\cdot\vec{r}}}{\sqrt{V}}$$

$$= \sum_{k'<k_F} \frac{e^{i\vec{k}'\cdot\vec{r}}}{V^{3/2}} \left(\int d^3r' \, \frac{e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}'-\vec{r})}}{|\vec{r}'-\vec{r}|}\right) \times e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

$$= \sum_{k'<k_F} \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} \left\{\frac{1}{V}\int d^3y \, \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{y}}}{y}\right\}$$ ~~(332)~~

$$= \left(\sum_{k'<k_F} Q(\vec{k}-\vec{k}')\right) \varphi_{\vec{k}}(\vec{r}) \quad \text{—} \ (333)$$

$$\& \quad -\frac{\nabla^2}{2}\varphi_{\vec{k}}(\vec{r}) = \frac{k^2}{2}\varphi_{\vec{k}}(\vec{r}) \quad \text{—} \ (334)$$

$\therefore$ $\varphi_{\vec{k}}(\vec{r})$ is indeed the eigenf of (332) as we posited

the eigen value is

$$\varepsilon(\vec{k}) = \frac{k^2}{2} + \sum_{\vec{k}'<k_F} \varphi(\vec{k}-\vec{k}') \quad \text{—} \ (335)$$

~~$\varphi(\vec{k}-\vec{k}') = \frac{1}{V}\int d^3y \, e^{i}$~~

$$\varphi(\vec{k}) = \frac{1}{V}\int d^3y \, \frac{e^{i\vec{k}\cdot\vec{y}}}{y} = \frac{4\pi}{Vk^2} \quad \text{— (336)}$$

(Show as H.W.)

Now,

$$\sum_{k' \le k_F} \varphi(\vec{k}-\vec{k}') \longrightarrow \frac{V}{(2\pi)^3}\int_{k' \le k_F} d^3k' \, \frac{4\pi}{V|\vec{k}'-\vec{k}|^2}$$

~~$\vec{\kappa} = \vec{k}' - \vec{k}$~~

$$= \frac{1}{(2\pi)^3}\int_{|\vec{\kappa}+\vec{k}| \le k_F} d^3\kappa \, \frac{4\pi}{\kappa^2}$$

~~$|\vec{\kappa}+\vec{k}|^2 \le k_F^2$~~

~~$\kappa^2 + k^2 + 2\vec{\kappa}\cdot\vec{k} \le k_F^2$~~

~~$\Rightarrow \vec{\kappa}\cdot\vec{k} \le \frac{k_F^2 - \kappa^2 - k^2}{2}$~~

~~$\kappa k \cos\theta \le \frac{k_F^2 - \kappa^2 - k^2}{2}$~~

~~$\text{or } \cos\theta \le \frac{k_F^2 - \kappa^2 - k^2}{2\kappa k}$~~

~~$= \frac{1}{2\pi^2}\int$~~

~~$= C \int 4\pi\kappa \int \sin\theta \, d\theta \int d\varphi$~~

$$= \frac{2}{\pi} k_F \, F\!\left(\frac{k}{k_F}\right) \quad \text{— (337)}$$

$$\text{where } F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right| \quad \text{— (338)}$$

$$\therefore \quad \varepsilon(\vec{k}) = \frac{k^2}{2} - \frac{k_F}{2\pi}\left\{ 2 + \frac{(k_F^2 - k^2)}{k k_F} \ln\left|\frac{k_F + k}{k_F - k}\right| \right\} \quad \text{— (339)}$$

Note that. $\varphi_{\vec{k}}(\vec{r})$ is also an eigen function if we ignore the exchange term.

The total HF energy of the electron gas can be computed ~~by~~ as

$$E_{HF} = N\left[\frac{3}{5}\varepsilon_F - \frac{3}{4}\frac{k_F}{\pi}\right] \quad \text{—} \quad (340)$$

(H.W.) Show the

Thus, the total energy per electron of the HEG can be written as:

$$\bar{\varepsilon} = \frac{E}{N} = \left[\frac{3}{5}\varepsilon_F - \frac{3}{4}\frac{k_F}{\pi}\right] \equiv \frac{1}{2}\times\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right] \text{Ha.} \quad \text{—} \quad (341)$$

where $r_s \rightarrow$ WS radius, $r_s = \left[\frac{3}{4\pi n}\right]^{1/3}$

Typically, r_s in metals ranges from 2 to 6. $\Rightarrow$ the exchange term (2nd term) in (341) cannot be ignored compared to the first term.

In the limit of high densities ($r_s \rightarrow 0$) an expansion of the exact g.s. energy of the HEG has been calculated

$$\bar{\varepsilon} = \frac{1}{2}\times\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \underbrace{0.0622\ln(r_s) - 0.096 + O(r_s)}\right] \text{Ha} \quad \text{—} \quad (342)$$

$\longleftarrow$ Correlation energy

$$\boxed{\varepsilon_{corr} \equiv \bar{\varepsilon}_{exact} - \varepsilon_{HF}} \longrightarrow (343)$$

Note that in this case

$$\left.\begin{aligned} \varepsilon_{kin} &= \varepsilon_{kin}(r_s) \\ \varepsilon_x &= \varepsilon_x(r_s) \\ \& \ \varepsilon_c &= \varepsilon_c(r_s) \end{aligned}\right\} \quad (344)$$

The average change in energy of an electron from the free & indep. value due to exchange is $\varepsilon_x = -\frac{3}{4}\frac{k_F}{\pi} = -\frac{0.916}{2r_s}$ Ha. — ③④⑤

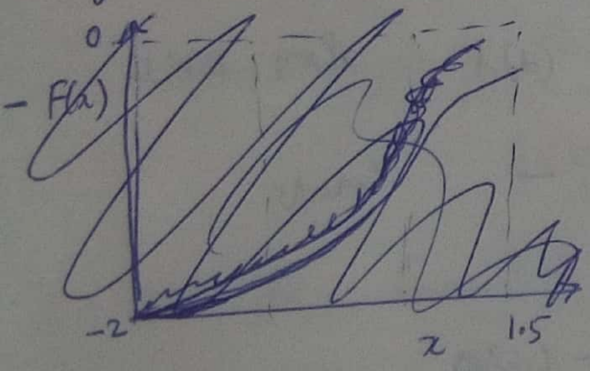
Slater suggested that in non-uniform systems and, in particular, in presence of periodic lattices, we could simplify the HF eqns. by replacing the exchange term by a local energy given by twice ε_x w/ k_F calculated from the local density

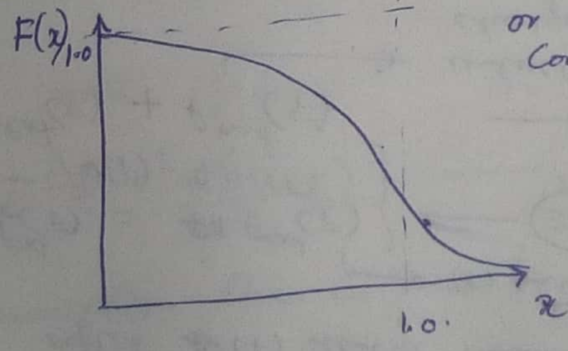
$$V_x^{\text{Slater}}(\vec{r}) = -\frac{0.916}{r_s} = -\underbrace{A}_{\text{constant}}\left(n(\vec{r})\right)^{1/3} \text{ Ha} \quad \text{— (346)}$$

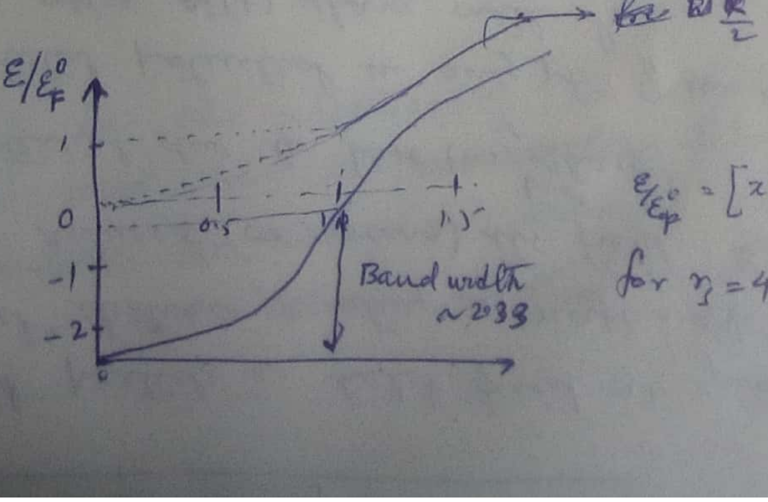
Note that this makes the exchange potential local like the Hartree potential.

It's a crude approximation but often used in calculations (DFT, particularly

E: There is log divergence in $\frac{d\varepsilon}{dk}$ around k_F. This is unphysical and a consequence of the divergence in the Coulomb interaction at $k=0$ (F.T.). Can be removed by having a gap (insulator) or using a screened Coulomb interaction.







exchange depresses the energies as well as increase the bandwidth. This effect is not seen in expts

$\varepsilon/\varepsilon_F^0 = [x^2 - 0.663\, r_s F$

for $r_s = 4$

~~[illegible]~~. Lec. 18. Thomas-Fermi method for screening in metal

Suppose a positively charged particle is held fixed at given position in ~~the~~ HEG. It will attract electrons, creating a surplus ~~of~~ (−) charge in its neighbourhood, which reduces (or screens) its field. ~~The for~~

Let $U^{ext}(\vec{r}) \rightarrow$ potential due to bare (+) test charge

$U(\vec{r}) \rightarrow$ total potential in any pt. of the HEG after (+) charge added.

(+) particle's charge density

Now, $$\left.\begin{aligned} -\nabla^2 U^{ext}(\vec{r}) &= 4\pi \rho^{ext}(\vec{r}) \\ -\nabla^2 U(\vec{r}) &= 4\pi \rho(\vec{r}) \end{aligned}\right\} \text{ — } ③④⑦$$

Total charge : $$\rho(\vec{r}) = \rho^{ext}(\vec{r}) + \underbrace{\rho^{ind}(\vec{r})}_{\text{induced charge}} \text{ — } ③④⑧$$

$$U^{ext}(\vec{r}) = \int d^3r' \, \epsilon(\vec{r}, \vec{r}') \, U(\vec{r}') \text{ — } ③④⑨$$

for HEG: $$\epsilon(\vec{r}, \vec{r}') \equiv \epsilon(\vec{r} - \vec{r}') \text{ — } ③⑤⓪$$

$$\therefore U^{ext}(\vec{r}) = \int d^3r' \, \epsilon(\vec{r} - \vec{r}') \, U(\vec{r}') \text{ — } ③⑤①$$

F.T. $\Rightarrow$ $$U^{ext}(q) = \epsilon(q) \, U(q) \text{ — } ③⑤②$$

where $$\epsilon(q) = \int d^3r \, e^{i\vec{q}\cdot\vec{r}} \, \epsilon(\vec{r})$$

$$\Rightarrow \boxed{U(\vec{q}) = \frac{U^{ext}(\vec{q})}{\epsilon(\vec{q})}} \text{ — } ③⑤③$$

Now, $\rho^{ind}(\vec{r}) = \int d^3r' \, \chi(\bar{r}-\bar{r}') \, U(\bar{r}')$ — (354)

(Linear response)

$\Rightarrow \rho^{ind}(\vec{q}) = \chi(\vec{q}) \, U(\vec{q})$ — (355)

F.T. of (347) [illegible] $\Rightarrow$

$$\left.\begin{aligned} q^2 U^{ext}(q) &= 4\pi \rho^{ext}(q) \\ q^2 U(q) &= 4\pi \rho(q) \end{aligned}\right\} \text{(356)}$$

Together w/ (355) this means that

$$\frac{q^2}{4\pi}\left(U(q) - U^{ext}(q)\right) = \rho^{ind}(\bar{r})$$

$$\Rightarrow U(q) = \frac{U^{ext}(q)}{1 - \frac{4\pi}{q^2}\chi(q)} \quad \text{— (357)}$$

Comparing w/ (353) we get

$$\epsilon(q) = 1 - \frac{4\pi}{q^2}\chi(q) \quad \text{— (358)}$$

Except for the L.R. assumption this is exact

Thomas-Fermi model:

To determine the charge density in the presence of the total potential $U = U^{ext} + U^{ind}$ we must solve the ~~one electron~~ Schr. eqn. (no exchange) as T-F did

- We can use the Hartree approximation for now

$U(\bar{r})$ takes the place of the ext + Hartree potential together (non-zero here bcos of the added charge)

$$-\frac{\nabla^2}{2}\varphi(\vec r) - U(\vec r)\varphi(\vec r) = \varepsilon\,\varphi(\vec r) \quad \text{— (359)}$$

Self-consistency can be imposed by requiring that $U(\vec r)$ yield an induced density $\rho^{ind}(\vec r)$: (353) & (357) are obeyed,

The Thomas-Fermi approach is based on the assumption that $U(\vec r)$ is so slowly varying that the free-$\bar{e}$ eigenvalues only change ~~by~~;

$$\varepsilon(\vec k) = \frac{k^2}{2} - U(\vec r) \quad \text{— (360)}$$

i.e. $\varepsilon(\vec k)$ at a pt $\vec r$ is only ~~only~~ changed by the local value of the potential. ($U(\vec r)$ must vary slowly on the scale of $\sim 1/k_F$

Thus we assume that solutions to (359) describe a set of electrons w/ energies of the simple classical form (360). To calculate the local charge density produced, we use (360) in the expression for the electronic number ~~charge~~ density at temperature T.

$$n(\vec r) = \int \frac{d^3k}{4\pi^3} \frac{1}{\exp\left[\beta\left(\frac{k^2}{2} - U(\vec r) - \mu\right)\right]+1} \quad \text{— (361)}$$

whereas the unperturbed density is:

$$n_0(\mu) = \int \frac{d^3k}{4\pi^3} \frac{1}{\exp\left[\beta\left(k^2/2 - \mu\right)\right]+1} \quad \text{— (362)}$$

∴ induced charge density is:

$$\rho^{ind}(\vec r) = -\left[n_0(\mu + U(\vec r)) - n_0(\mu)\right] \quad \text{— (363)}$$

This is the basic equation of non-linear TF theory.

If we assume $U(\vec{r})$ is small (compared to $k_B T$) then we can expand (363) to leading order and write:

$$\rho^{ind}(\vec{r}) \simeq -\left.\frac{\partial n_0}{\partial \mu}\right|_{\mu} U(\vec{r}) \quad \text{—} \quad (364)$$

Comparing this w/ (354) & (355) we get

$$\chi(\vec{q}) = -\left(\frac{\partial n_0}{\partial \mu}\right) \quad \text{—} \quad (365)$$

i.e. it is independent of $\vec{q}$.

From (358) we get for the static dielectric constant.

$$\epsilon(q) = 1 + \frac{4\pi}{q^2}\left(\frac{\partial n_0}{\partial \mu}\right) \quad \text{—} \quad (366)$$

We define the T-F wave vector $k_{TF}^2 = 4\pi\left(\frac{\partial n_0}{\partial \mu}\right)$ — (367)

$$\Rightarrow \quad \epsilon(q) = 1 + \frac{k_{TF}^2}{q^2} \quad \text{—} \quad (368)$$

To see the significance of k_{TF}, let $U^{ext}(\vec{r}) = \frac{Q}{r}$ — (369)

$$\Rightarrow \quad U^{ext}(\vec{q}) = \frac{4\pi Q}{q^2} \quad \text{—} \quad (370)$$

$$\Rightarrow \quad U(\vec{q}) = \frac{1}{\epsilon(q)} U^{ext}(q) = \frac{4\pi Q/q^2}{1 + k_{TF}^2/q^2} = \frac{4\pi Q}{q^2 + k_{TF}^2} \quad \text{—} \quad (371)$$

$$\Rightarrow \quad \boxed{U(\vec{r}) = \frac{Q}{r} e^{-k_{TF} r}} \quad \text{—} \quad (372)$$

i.e. the total potential is a screened Coulomb potential which dies exponentially over the length scale $\sim 1/k_{TF}$

For e.g. when $T \ll T_F$ $\quad \frac{\partial n_0}{\partial \mu} \approx$ density of states a $\mathcal{E}_F = D(\mathcal{E}_F)$

$$= k_F/\pi^2 \quad \text{—} \quad (3.73)$$

$$\Rightarrow \frac{k_{TF}^2}{k_F^2} = \left(\frac{16}{3\pi^2}\right)^{2/3} r_s \quad \text{—} \quad (3.74)$$

$$\Rightarrow k_{TF} = \frac{2.95}{r_s^{1/2}} \text{Å}^{-1} \quad \text{—} \quad (3.75)$$

For $r_s = 2-6$ at metallic densities $k_{TF} \sim k_F \sim$ interparticle spacing

Thus, the sea of electrons is extremely effective in shielding.

TF theory doesn't explain Friedel oscillations seen in metals and doesn't work for strongly varying external potentials (atoms/molecules) has been used.

However, there is an interesting aspect that has been used.

The approximation assumed a self-consistency between charge & potential implying that the ~~Hartree potential which results~~ ~~from ex [illegible], can be~~ energy of the "inhomogeneous" electron gas can be treated as a functional of the electron density $n(\vec{r})$. While it was realised in an ad-hoc manner here it is possible to put this idea on a stronger footing. This is what we shall do w/ DFT.

Note that w/ the Coulomb potential screened we can go back to the HF treatment & replace the $1/k^2$ term in the exchange by $1/\epsilon(k)k^2$ which will remove the divergence seen ~~at~~ k_F. $\Rightarrow$ screening reduces the importance of e-e interaction.

/2/2018 Lec. 19 Building up to DFT

Correlation energy for HEG : $\mathcal{E}_c \equiv \mathcal{E}_{exact} - \mathcal{E}_{HF}$ — (376)

Thus to estimate $\mathcal{E}_c$ we need to know the exact energy. But an analytic solution of the full interacting problem is not accessible. Wigner proposed interpolating the results between $r_s \to 0$ & $r_s \to \infty$ limits.

At low density ($r_s \to 0$) electrons form the so-called Wigner crystal and the correlation energy is just the electrostatic energy of pt. charge on the b.c.c. lattice. Wigner proposed the following formula:

$$\mathcal{E}_c = -\frac{0.44}{r_s + \cancel{0}7.8} \quad (\text{in } Ha) \longrightarrow (377)$$

Gellman & Brueckner, through MBPT methods calculated the correlation energy exactly in the high-density ($r_s \to 0$) limit. For a spin unpolarized gas ($N_\uparrow = N_\downarrow$) their result was:

$$\mathcal{E}_c(r_s) \to 0.0311 \ln r_s - 0.048 + r_s (A \ln r_s + C) + \cdots \quad \text{— (378)}$$

The $\ln(r_s)$ terms are the sources of non-analyticity. At low densities ($r_s \to \infty$) the system can be considered a Wigner crystal w/ zero pt. motion leading to

$$\mathcal{E}_c(r_s) \to \frac{a_1}{r_s} + \frac{a_2}{r_s^{3/2}} + \frac{a_3}{r_s^2} + \cdots \quad \text{— (379)}$$

The most accurate estimates of $\mathcal{E}_c$ are due to Quantum Monte Carlo calculation (e.g. Ceperley-Adler 1980) at various r_s. The result have since been parametrized by several others and are employed in practical calculations. [Perdew & Zunger (PZ); Vosko, Wilkes & Nussair (VWN)].

So the energy per particle can be written as:

$$\mathcal{E}_{exact}(r_s) = \mathcal{E}_{HF}(r_s) + \mathcal{E}_c(r_s) \quad \text{—— (380)}$$

Note that the energies are dependent on the densities n,

The Thomas-Fermi-Dirac Functional :

The Thomas-Fermi approximation involved assuming that the local energy of a perturbed e^- gas can be written in terms of the energy of a free-gas w/ the density equalling the density in the perturbed gas. Since the free gas only has kinetic energy in the absence of interaction, this basically means that the kinetic energy of the perturbed gas was approximated this way.

Kinetic Energy per electron in a HEG $= \frac{3}{5}\epsilon_F = \frac{3}{10}k_F^2 = \frac{9\pi^2}{10}n^{2/3} = \epsilon_{kin}(n)$

$\therefore$ K.E. per electron in a perturbed HEG in T-F approx.:

$$\cancel{\epsilon_k^{TF}(n(\vec r))} = \left(\frac{9\pi^2}{10}\right)(n(\vec r))^{2/3} \equiv C_1 (n(\vec r))^{2/3} \quad \text{— (381)}$$

Further, they assumed the electrons may interact w/ an external field $V_{ext}(\vec r)$ while their mutual interaction can be written in classical terms as

$$E_{int} = \frac{1}{2}\int d^3r \int d^3r' \frac{n(\vec r)\,n(\vec r')}{|\vec r - \vec r'|} \quad \text{— (382)}$$

This is just the Hartree approx. Thus, we get

$$V(\vec r) = V'_{ext}(\vec r) + \int d^3r' \frac{n(\vec r')}{|\vec r - \vec r'|} \quad \text{— (383)}$$

The K.E. density $= \epsilon_k^{TF} = n(\vec r)\,\epsilon_k^{TF}(n(\vec r)) = C_1 (n(\vec r))^{5/3}$ — (384)

$$\therefore \quad E_{TF}[n(\vec r)] = \int d^3r\, n(\vec r) \left[\epsilon_k^{TF}(n(\vec r)) + V_{ext}(\vec r) + V_H(\vec r)\right\} \quad \text{— (385)}$$

Dirac added his exchange term to this:

$$\epsilon_x(n(\vec r)) = C_2\, n^{4/3} \times n(\vec r) = C_2\, n(\vec r)^{4/3} \quad \text{— (386)}$$

$$\therefore \quad E_{TF}[n(\vec r)] = C_1 \int d^3r\, (n(\vec r))^{5/3} + \int d^3r\, V_{ext}(\vec r)\, n(\vec r) + C_2 \int d^3r\, n(\vec r)^{4/3} + \frac{1}{2}\int d^3r \int d^3r' \frac{n(\vec r)\,n(\vec r')}{|\vec r - \vec r'|}$$

Thus, the g.s. energy of an inhomogeneous interacting e^- gas can be written as a functional of the density (approximately).

The idea of the density as a basic variable is profound as it obviates the need for the cumbersome wavefunction. Indeed in 1965, ~~the~~ Hohenberg and Kohn showed that the ground-state energy is a functional of the single particle density. This was the birth of DFT – a new way to do QM of many-electron systems.

The Hohenberg-Kohn Theorems :

Usual QM: $H\Psi = E\Psi$, $H = \hat{T} + \hat{V}_{ext} + \hat{W}$

where $\hat{V}_{ext} = \sum_i \hat{v}_{ext}(\hat{\vec{r}}_i)$ ⟶ nuclear attraction plus external fields.

$\hat{W} = \sum_{i<j} \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|}$ for e^-s.

— (387)

We know V_{ext} & W and determine Ψ by solving the Schrödinger eqn

$\Psi \equiv \Psi(x_1, x_2 \cdots x_N)$ $x = (\vec{r}, \sigma)$ → (388)

B· 4N dimensional object.

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \text{— (389)}$$

Any property $Q = \frac{\langle \Psi | \hat{Q} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

For a given kind of ~~system~~ particles $\hat{W}$ is fixed, & of course, $\hat{T}$ is also fixed. So what really decides the $\hat{H}$ is $\hat{V}_{ext}$. Thus we can say that for a given kind of particles (w/ a specified interaction)

$$\hat{V}_{ext} \Rightarrow \hat{H} \Rightarrow \Psi \Rightarrow E, Q \cdots \quad \text{— (390)}$$

In particular, $\hat{V}_{ext} \Rightarrow n(x) = N \int dx_2 \cdots dx_N |\Psi(x_1, x_2 \cdots x_N)|^2$ — (391)

For simplicity let's first consider spinless particles. Then,

$$n(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r}_2, \vec{r}_3 \ldots \vec{r}_N)|^2 d^3r_2 \ldots d^3r_N \quad \text{—} \; \textcircled{392}$$

<u>Theorem 1</u>: For any system of interacting particles in a external potential $\hat{V}_{ext}(\vec{r})$, the potential $\hat{V}_{ext}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\vec{r})$.

<u>Corollary 1</u>: Since the Hamiltonian is thus fully determined (except for a constant shift), it follows that many-body wavefns. for all states (ground & excited) are determined. Therefore, <u>all properties</u> of the system are completely determined given only the g.s. density $n_0(\vec{r})$

~~Theorem 2: A universal functional:~~

$$n_0(\vec{r}) \Rightarrow V_{ext}(\vec{r}) \Rightarrow \hat{H} \Rightarrow \{\Psi\} \Rightarrow \text{All properties}$$

$$\Rightarrow \text{in particular} \quad E \equiv E[n_0(\vec{r})] \quad \text{—} \; \textcircled{393}$$

<u>Theorem 2</u>. A <u>universal functional</u> for the energy in terms of the density $n(\vec{r})$ can be defined, valid for any external potential $V_{ext}(\vec{r})$. For any particular $V_{ext}(\vec{r})$, the exact g.s. energy of the system is the global minimum value of this functional, & the density $n(\vec{r})$ that minimizes the energy functional is the g.s. density.

<u>Corollary 2</u>: $E[n]$ alone is sufficient to determine the exact g.s. energy & density. In general, excited states must be determined by other means.

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Proof of Theorem 1: (density as a basic variable)

Let's prove by contradiction as was originally done. Let $V_{ext}^{(1)}(\vec r)$ & $V_{ext}^{(2)}(\vec r)$ be two potentials that differ by more than a constant & yet lead to the same g.s. density $n(\vec r)$. They correspond to 2 diff. Hamiltonians $\hat H^{(1)}$ & $\hat H^{(2)}$, which have ground states $\Psi^{(1)}$ & $\Psi^{(2)}$, respectively, wh[?] are hypothesized to have the same g.s. density $n_0(\vec r)$. Further, we assume that the g.s. of both systems are non-degenerate. (This condition can be relaxed)

Now, from the variational theorem, we have:

$$E^{(1)} = \langle \Psi^{(1)} | \hat H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat H^{(1)} | \Psi^{(2)} \rangle \quad \text{— (394)}$$

The strict inequality follows because of the non-degenerate nature of the states.

Using the defn. of $\hat H^{(1)}$ we have

$$E^{(1)} < \langle \Psi^{(2)} | (\underbrace{\hat T + \hat V_{ext}^{(2)} + \hat W}_{\hat H^{(2)}}) | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat V_{ext}^{(1)} | \Psi^{(2)} \rangle$$

$$\text{i.e. } E^{(1)} < E^{(2)} + \int d^3r\, n_0(\vec r) \left(\hat V_{ext}^{(1)}(\vec r) - V_{ext}^{(2)}(\vec r) \right) \quad \text{— (395)}$$

Ill'y starting from $\hat H^{(2)}$, instead, we can show that

$$E^{(2)} < E^{(1)} + \int d^3r\, n_0(\vec r) \left(\hat V_{ext}^{(2)}(\vec r) - V_{ext}^{(1)}(\vec r) \right) \quad \text{— (396)}$$

~~(395) - (396) ⇒ $(E^{(1)} - E^{(2)}) < (E^{(2)} - E^{(1)}) + \int d^3r\, n(\vec r) \left(V_{ext}^{(1)} - V_{ext}^{(2)} \right)$~~

(395) + (396) ⇒ $E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$ — (397)

This is a contradiction. Hence the original hypothesis, that is 2 different ext. potentials yield the same g.s. density, must be wrong. Therefore, the Theorem 1 is proved.

The corollary easily follows. For a given g.s. density there c'd be many Ψ's possible. But the g.s. Ψ is the one that minimizes the energy. This fixes the relation between $n_0(\vec{r})$ & Ψ.

$$\Rightarrow \quad E \equiv E[n_0] \;,\; \Psi \equiv \Psi[n_0], \;\ldots$$

This theorem doesn't tell us any practical way to obtain either the functionals or the g.s. density itself. This is the job of the second theorem.

Proof of second theorem: To define a functional we need to first identify the space of densities involved. From the proof of the first theorem it is clear that we are talking about g.s. densities that arise from some external potentials $v_{ext}(\vec{r})$. Such densities are called V-representable densities. The space of such densities is the mapped to real numbers, viz the energy. Now, if we specify $n(\vec{r})$ as the g.s. density then the first theorem assures us that $\Psi_0 \equiv \Psi[n]$

$$\left.\begin{aligned} \Rightarrow \quad \text{Kinetic energy} &= \langle \Psi[n] | \hat{T} | \Psi[n] \rangle \equiv T[n] \\ \text{Interaction energy} &= \langle \Psi[n] | \hat{W} | \Psi[n] \rangle = E_{int}[n] \end{aligned}\right\} \text{— } ③⑨⑧$$

$\therefore$ The total energy also becomes a functional,

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d^3r \, n(\vec{r}) \, v_{ext}(\vec{r}) \left(+ E_{II} \right) \quad \text{— } ③⑨⑨$$

$\downarrow$ ion-ion interaction

We define $F_{HK}[n] \equiv T[n] + E_{int}[n]$ — (400)

Since, for a given kind of particles w/ a ~~gre~~ specified interaction, the $\hat{T}$ & $\hat{W}$ operators are fixed

$F_{HK}[n]$ becomes a universal functional applicable to all such systems irrespective of the external potential. i.e. the same functional (formula) can be used for any N-particle system of particles interacting the same way. In this course we will deal only w/ electrons. So $F_{HK}[n]$ is the same for all interacting N electron systems. We c/d also consider, as we shall shortly, all non-interacting N electron system which will then have their own F_{HK}.

Now, let system 1 have a g.s. density $n^{(1)}(\bar{r})$ corresponding to an external potential $v_{ext}^{(1)}(\bar{r})$.

$$\Rightarrow \quad E^{(1)} = E_{HK}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle \quad \text{— (401)}$$

Now consider a different density $n^{(2)}$, which necessarily corresponds to a different wavefn. $\Psi^{(2)}$. It follows immediatily that energy $E^{(2)}$ of the state is greater than $E^{(1)}$,

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} \quad \text{— (402)}$$

In other words, using any other density in the functional yields an energy necessarily higher than that yielded when using the g.s. density:

$$E_{HK}[n_0] \leq E_{HK}[n] \quad \forall\, n \in \text{V-rep.} \quad \text{— (403)}$$

It follows then that if $F_{HK}[n]$ was known then the g.s. energy can be obtained by minimizing $E_{HK}[n]$ w/ respect to n. The minimizing n has to be n_0 by (403). This proves the second theorem & corollary 2 since only g.s. properties are predicted.

Constrained Search Formulation of DFT – Levy-Lieb.

We know that (for all normalized Ψ)

$$E = \min_{\Phi} \langle \Psi | \hat{H} | \Psi \rangle \quad \text{——} \quad (404)$$

First let's define a space of all N-electron Ψ that yield the same density $n(\vec{r})$: $\{\Psi \to n(\vec{r})\}_N$ — (405)

If we first minimize the expectation value over this space we have :

$$E_{LL}[n] \equiv \min_{\Psi \to n(\vec{r})} \left\{ \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \int d^3r \, v_{ext}(\vec{r}) \, n(\vec{r}) \right\} \quad (+ E_{II})$$

$$\equiv F_{LL}[n] + \int d^3r \, v_{ext}(\vec{r}) \, n(\vec{r}) \quad (+ E_{II}) \quad \text{—} (405)$$

Now we minimize $E_{LL}[n]$ over all ~~densities~~ such densities integrating to N which were obtained from N-electron wfn. Such a space is called N-representable. We get back (404)

$$E = \min_{n(\vec{r})} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \right\}$$

$$\equiv \min_{n(\vec{r})} \left\{ F_{LL}[n] + \int d^3r \, v_{ext}(\vec{r}) \, n(\vec{r}) \right\} \quad (+ E_{II}) \quad \text{—} (406)$$

where the Levy-Lieb universal functional is defined as

$$F_{LL}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \quad \text{—} (407)$$

In this form $E_{LL}[n]$ is manifestly a fn.al of $n(\vec{r})$ & the g.s. is found by minimizing E_{LL}. Both theorems are proven in one shot. But the advantage is that it not only clarifies the meaning of the functional but also

provides a way to calculate $F_{LL}[n]$: minimizing $\hat{T} + W$ over all N-electron wavefns yielding the density $n(\vec{r})$.

It also extends the validity of the theor