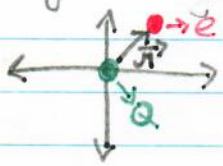
1. Introduction to correlated many-body systems

⊖ One-body problem: Single particle in an external field!

Example: Electron in electric field of a static point charge Q!

$$H = \frac{\vec{p}^2}{2m} - \frac{Qe}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|} \quad (1)$$

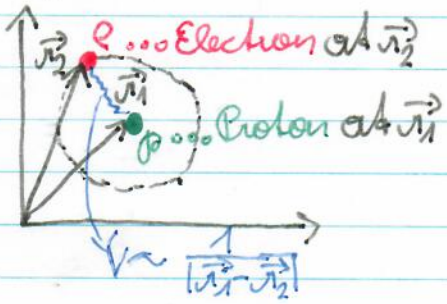


⇒ „Easy" to solve!

⊖ Two-body problem: Two interacting particles!

Example: Hydrogen atom:

$$H = \frac{\vec{p}_1^{\,2}}{2m_p} + \frac{\vec{p}_2^{\,2}}{2m_e} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (2)$$



Interaction between 2 dynamic particles!

⇒ „Difficult" to solve!

But: For 2 particles a reduction to one-body problem is possible by a canonical transformation to center-of-mass and relative coordinates!

Total mass: $M = m_p + m_e$ Reduced mass: $m = \frac{m_p m_e}{m_p + m_e}$

$$\left\{ \begin{aligned} \vec{r}_1 &= \vec{R} - \frac{m_e}{M}\vec{r} \\ \vec{r}_2 &= \vec{R} + \frac{m_p}{M}\vec{r} \\ \vec{p}_1 &= \frac{m_p}{M}\vec{P} - \vec{p} \\ \vec{p}_2 &= \frac{m_e}{M}\vec{P} + \vec{p} \end{aligned} \right\} \Leftrightarrow \left\{ \begin{aligned} \vec{R} &= \frac{m_p\vec{r}_1 + m_e\vec{r}_2}{M} \quad \text{... Center-of-mass coord.} \\ \vec{r} &= \vec{r}_2 - \vec{r}_1 \quad \text{... Relative coord.} \\ \vec{P} &= \vec{p}_1 + \vec{p}_2 \\ \vec{p} &= \frac{m_p}{M}\vec{p}_2 - \frac{m_e}{M}\vec{p}_1 \end{aligned} \right\} \quad (3)$$

$$\Rightarrow H = \boxed{\frac{\vec{P}^2}{2M}} + \boxed{\frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|}} \quad (4)$$

Free motion of the center of mass

Single particle problem in a central potential for the relative coordinate [cf. Eq(1)]

⊖ Three- and more-body problem:

⇒ Three or more **interacting** particles!

⇒ Generic case for real physical systems!

Examples: Nuclear matter, (classical) liquids, electrons in atoms and solids, ...

• Electrons in an atom: (in center-of-mass coord.)

$$H = \underbrace{\sum_{i=1}^{Z}\left[\frac{\vec{p}_i^{\,2}}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_i|}\right]}_{H_0} + \underbrace{\sum_{i<j=1}^{Z}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_i-\vec{r}_j|}}_{H_I} \quad (5)$$

(m ↳ reduced mass)

Z ... atomic number = number of electrons for a neutral atom

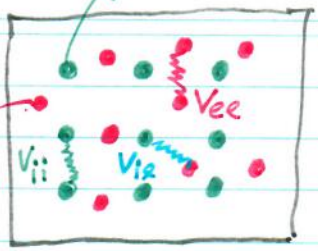
(mass polarization term $\frac{1}{m_N}\sum_{i<j=1}^{Z}\vec{p}_i\vec{p}_j$ has been neglected)

H_0 ... Non-interacting electrons in the field of the nucleus

H_I ... Interactions between the electrons

electrons ~ $O(10)$ - $O(100)$

Electrons in a solid: ⇒ # electrons ~ 10^{23}



$$H = \sum_{i=1}^{N_i} \frac{\vec{P}_i^2}{2M_i} + \sum_{i<j=1}^{N_i} V_{ii}(\vec{R}_i - \vec{R}_j) \Rightarrow H_{lattice}$$

$$+ \sum_{i=1}^{N_i} \sum_{j=1}^{N_e} V_{ie}(\vec{R}_i - \vec{r}_j) \Rightarrow H_{lattice\text{-}electron}$$

$$+ \sum_{i=1}^{N_e} \frac{\vec{p}_i^2}{2m_e} + \sum_{i<j=1}^{N_e} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} \Rightarrow H_{electron}$$

$\vec{P}_i$ ... momentum of ion
$\vec{R}_i$ ... position of ion
M_i ... mass of ion

$\vec{p}_i$ .. momentum of electron
$\vec{r}_i$ .. position of electron
m_e .. mass of electron

V_{ii} .. ion-ion interaction
V_{ie} .. ion-electron interaction

$\frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|}$ ... electron-electron Coulomb interaction (6)

Correlations ⇐

Simplification: Assume that lattice ions are fixed at their equilibrium position = Born-Oppenheimer approx.

$\Rightarrow \vec{P}_i = 0 \quad \vec{R}_i = \vec{R}_i^0$ (equilibrium position)

$$\Rightarrow \boxed{H = \underbrace{\sum_{i=1}^{N_e} \left[\frac{\vec{p}_i^2}{2m_e} + \sum_{j=1}^{N_i} V(\vec{R}_j^0 - \vec{r}_i) \right]}_{H_0 \,\hat{=}\, \text{kinetic energy}} + \underbrace{\sum_{i<j=1}^{N_e} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{H_I \,\hat{=}\, \text{potential energy}}} \quad (7)$$

⇒ Main topic of this lecture!!

⇒ Quantum mechanical and statistical description of non-interacting many-body systems:

→ N-particle Hilbert space: $\mathcal{H}_N = \mathcal{H}_1^{(1)} \otimes \dots \otimes \mathcal{H}_1^{(N)}$ (8)
($\mathcal{H}_1^{(i)}$ single-particle Hilbertspace of i^{th} particle)

→ N-particle Hamilton Operator: $H_N = H^{(1)} + \dots + H^{(N)}$ (9)
(for non-interacting particles) ⇒ $H^{(i)}$ acts in subspace $\mathcal{H}_1^{(i)}$

→ N-particle eigen-state: $|\psi\rangle_{(N)} = |\varphi_{(1)}\rangle_{(1)} \otimes \dots \otimes |\varphi_N\rangle_{(N)}$ (10)
One particle (eigen) state of the i^{th} particle; (N) → number of particle

For N identical particles ⇒ $[P_N^{\pi}, H_N] = 0$ (11) $(\mathcal{H}_1^{(i)} = \mathcal{H}_1^{(1)} \Leftrightarrow \mathcal{H}_N = (\mathcal{H}_1^{(1)})^N)$

P_N^{π} ... Permutation operator → Common eigenstates of H_N and P_N^{π} !

$\pi \in S_N$ = group of all permutations of the numbers 1 ... N (= symmetric group)

Each permutation π can be represented as sequence of transpositions T_{ij} two particls $i \leftrightarrow j$.

$\Rightarrow$ inverse of a transposition: $(T_{ij})^{-1} = T_{ij} \Rightarrow (T_{ij})^2 = \mathbb{1}$ (12)

$\Rightarrow$ Eigenvalues of T_{ij}: ± 1 $\Rightarrow$ Eigenvalues of $P_N^\pi = \pm 1$

$\Rightarrow$ N- particle state is symmetric or antisymmetric under permutation P_N^π:

$$|\psi\rangle_N = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} (\pm 1)^\pi \; |\varphi_{\pi(1)}\rangle_{(1)} \otimes \dots \otimes |\varphi_{\pi(N)}\rangle_{(N)} \qquad (13)$$

$(-1)^\pi = \pm 1$ for an even (odd) number of transpositions

$(\pm 1)^\pi$ → symmetric wave function $\Rightarrow$ BOSON'S

→ antisymmetric wave functions $\Rightarrow$ FERMION'S (Slater determ.)

$\Rightarrow$ Many Body problem reduces to one-body problem!

For a very large number of particles $N \sim 10^{23}$ (as in real materials)

$\Rightarrow$ (quantum) **statistical** methods can be applied!

Example: Grand canonical ensemble:

Partition function: $$Z(\beta, V, \mu) = \prod_i \sum_{n=0}^{\infty/1} e^{-\beta(\varepsilon_i - \mu)n} \quad (14)$$

(Bosons: ∞, Fermions: 1; n = occupation of state ε_i; i ↳ one-particle states)

ε_i ... eigenenergy of one-particle eigenstate $|\varphi_i\rangle$!

$\beta = \frac{1}{k_B T}$ (inverse temperature, k_B ... Boltzmann constant)

From $Z(\beta, V, \mu)$ $\Rightarrow$ Thermodynamic observables, e.g.: $$\frac{\langle N \rangle}{V} = n = \frac{1}{\beta} \frac{\partial \ln Z(\beta, V, \mu)}{\partial \mu} \quad (15)$$

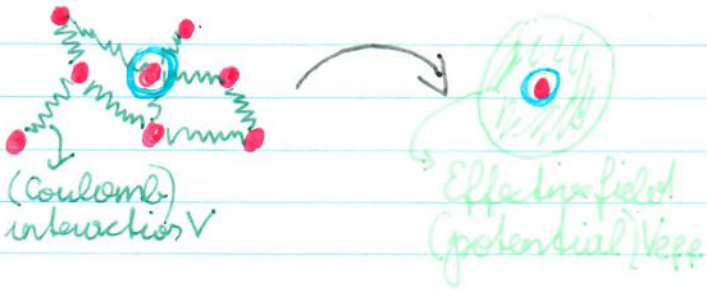
↳ average density!

e.g.: non-interacting electrons in a d-dimensional box:

$$\varepsilon_i = \varepsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m} \quad (16), \qquad n = \underbrace{2}_{\text{Spin}} \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d (\hat{=} \mathbb{Z}_i)} d^d k \, \frac{1}{1 + e^{\beta(\varepsilon_{\vec{k}} - \mu)}} \underset{T=0 \, (\beta=\infty)}{=} 2 \frac{\left(\frac{m\mu}{2\pi\hbar^2}\right)^{d/2}}{\Gamma(1 + \frac{d}{2})} \quad (17)$$

⊖ With interactions? ⇒ First step: Mean-field-like approaches

Basic idea:



⇒ Effect of the Coulomb interaction V onto a given electron ⊙ is replaced by an effective field V_{eff}, which is generated by all other electrons!

⇒ One-body problem for my single electron ⊙ in the field V_{eff}

⇒ ⊙ contributes to the mean field V_{eff} for the other electrons:

⇒ Selfconsistency problem: $V_{eff} = V_{eff}[\varphi^{(1)}]$

Schrodinger Eq.: $\varphi^{(1)}$ from V_{eff}

$$\left[\frac{\vec{p}^2}{2m} + V_{eff}\right]\varphi^{(1)} = E\,\varphi^{(1)} \quad (18)$$

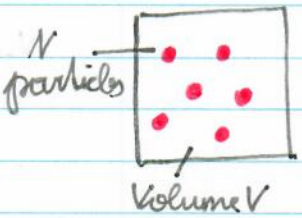
(Schrodinger Eq.)

Effective potential V_{eff} from $\varphi^{(1)}$ single particle wave function

also possible: $V_{eff} = V_{eff}[n]$, $n = |\varphi^{(1)}|^2$

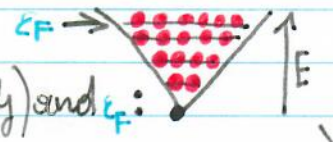
↳ density

⊙ Thomas - Fermi theory:



Non-interacting electrons in a box:

At $T=0$ ⇒ Energy levels are filled, until Fermi energy ε_F is reached!



⇒ Relation between number of particles/volume $n = \frac{N}{V}$ (density) and ε_F:

$$n = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_F^{3/2} = \frac{k_F^3}{3\pi^2} \quad (19)$$

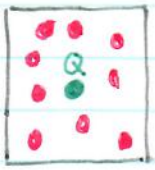
$\left(\varepsilon(k) = \frac{\hbar^2 k^2}{2m}\right.$ for free electrons$\left.\right)$

⇒ Energy as a function of density: $\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = \frac{\hbar^2}{2m}k_F^2$ (20)

Energy of particle at the Fermi level: $E_0 = \varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$ (21)

Assumption: This relation is also valid for interacting electrons
(Note: without external perturbation → homogeneous system → n constant)

Adding a perturbation: additional (positive) charge Q at the origin.



⇒ Redistribution of electrons ⇒ $n = n(\vec{r})$ and accordingly: $k_F = k_F(\vec{r})$

⇒ New charge distribution generates effective potential $V(\vec{r})$ for each electron (including the potential of the central charge Q!).

⇒ Total energy of electron at the Fermi level: $$E_0 = \frac{\hbar^2}{2m}\left(3\pi^2 n(\vec{r})\right)^{2/3} + V(\vec{r}) \quad (23)$$

⇒ From classical electrodynamics we obtain a second relation between $n(\vec{r})$ and $V(\vec{r})$ (Poisson equation):

$$\Delta\phi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon_0}$$

$\rho(\vec{r})$ .... charge density $\rho(\vec{r}) = -e\,n(\vec{r})$

$\phi(\vec{r})$ .... electrostatic potential: $V(\vec{r}) = -e\,\phi(\vec{r})$

Poisson equation for $V(\vec{r})$:

$$\Delta V(\vec{r}) = -\frac{e^2}{\varepsilon_0} n(\vec{r}) + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r}) + \frac{\rho_0 e}{\varepsilon_0} \quad (23)$$

↓ electron charge density; ↓ additional (point) charge at origin; ↓ homogeneous external charge (see below)

From Eq. (1) we can now express $n(\vec{r})$ in terms of $V(\vec{r})$:

$$n(\vec{r}) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E_0 - V(\vec{r})\right)^{3/2} \quad (24)$$

⇒ Inserting this expression for $n(\vec{r})$ into Eq. (23) gives a non-linear partial differential equation for $V(\vec{r})$:

$$\Delta V(\vec{r}) = -\frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E_0 - V(\vec{r})\right)^{3/2} + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r}) + \frac{\rho_0 e}{\varepsilon_0} \quad (24)$$

E_0 and ρ_0 depend on the specific situation to which the Thomas-Fermi theory is applied (see below)!

(a) Neutral atom: $Q = Z \cdot e$ Energy levels in hydrogen ↑

$\rho_0 = 0$ ... no additional external charge $E_0 = 0 \dots E_n \sim \frac{1}{n^2} \xrightarrow{n\to\infty} 0$

$$\Rightarrow \Delta V(\vec{r}) = -\frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[-V(\vec{r})\right]^{3/2} + \frac{Ze^2}{\varepsilon_0}\delta^{(3)}(\vec{r}) \quad (25)$$

SO(3) symmetry of the atom $\Rightarrow V(\vec{r}) = V(|\vec{r}|) = V(r)$

Ansatz: $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\varphi(r) \Rightarrow \Delta V(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\left[\underbrace{\left(\Delta\frac{1}{r}\right)}_{-4\pi\delta^{(3)}(\vec{r})}\varphi(r) + \frac{1}{r}\Delta\varphi(r) - \frac{2}{r^2}\frac{\partial\varphi}{\partial r}(r)\right]$ (26)

$$\Rightarrow \underbrace{\frac{Ze^2}{\varepsilon_0}\delta^{(3)}(\vec{r})\varphi(r)}_{=\delta^{(3)}(\vec{r})\varphi(0)} - \frac{Ze^2}{4\pi\varepsilon_0}\left[\frac{1}{r}\Delta\varphi(r) - \frac{2}{r^2}\frac{\partial\varphi}{\partial r}(r)\right] = -\frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^{3/2}\left[-4\pi\delta^{(3)}(\vec{r})\varphi(r) + \frac{1}{r}\varphi(r)\right]^{3/2} + \frac{Ze^2}{\varepsilon_0}\delta^{(3)}(\vec{r}) \quad (27)$$

These terms cancel if we assume the boundary condition $\boxed{\varphi(0) = 1}$

$\Rightarrow$ Reasonable, because at $r = 0$ there are no electrons and we should recover the potential of the nucleus!

We then consider Eq. (6) for $r > 0 \Rightarrow \delta^{(3)}(\vec{r})$ drops.

In spherical coordinates we have: $\Delta \triangleq \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$

$$\Rightarrow -\frac{Ze^2}{4\pi\varepsilon_0}\left[\frac{1}{r}\varphi''(r) + \frac{2}{r^2}\varphi'(r) - \frac{2}{r^2}\varphi'(r)\right] = -\frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^{3/2}\frac{\varphi(r)^{3/2}}{r^{3/2}}$$

$$\Rightarrow \varphi''(r) = \frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^{1/2}\frac{\varphi(r)^{3/2}}{r^{1/2}} \Rightarrow \varphi''(r) = \frac{1}{3\pi^2}\frac{4\pi}{2}(2Z)^{3/2}\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)^{3/2}\frac{\varphi(r)^{3/2}}{r^{1/2}}$$

Bohr's radius: $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$

$$\Rightarrow \varphi''(r) = \frac{8\sqrt{2}}{3\pi}\sqrt{Z}\,\frac{1}{a_0^{3/2}}\frac{\varphi(r)^{3/2}}{\sqrt{r}} \quad (28) \qquad r = a_0\left(\frac{3\pi}{8\sqrt{2Z}}\right)^{2/3}x$$

$$\varphi(r) = \chi(x(r)) \rightarrow \varphi''(r) = \chi''(x)\left(\frac{dx}{dr}\right)^2 = \chi''(x)\,a_0^{-2}\left(\frac{3\pi}{8\sqrt{2Z}}\right)^{-4/3}$$

$$\Rightarrow a_0^{-2}\left(\frac{3\pi}{8\sqrt{2Z}}\right)^{-4/3}\chi''(x) = \left(\frac{3\pi}{8\sqrt{2Z}}\right)^{-1}a_0^{-3/2}\frac{\chi(x)^{3/2}}{a_0^{1/2}\left(\frac{3\pi}{8\sqrt{2Z}}\right)^{1/3}\sqrt{x}}$$

$$\Rightarrow \boxed{\chi''(x) = \frac{\chi(x)^{3/2}}{\sqrt{x}}, \quad \chi(0) = 1} \quad (29)$$

$\Rightarrow$ Universal Thomas-Fermi equation (independent of physical parameters)!

1. Boundary condition : $\chi(0) = 1$
2. Boundary condition : ?

$\Rightarrow$ For neutral atom: Total number of electrons = Z.

$$\Rightarrow \int_{\mathbb{R}^3} d^3r\, n(\vec{r}) = 4\pi \int_0^\infty dr\, r^2 n(r) = Z$$

From Eq. (23) and (26) we obtain: $n(r) = \frac{Z}{4\pi r}\varphi''(r)$

$$\Rightarrow 4\pi \int_0^\infty dr\, r^2 n(r) = Z \int_0^\infty dr\, r\, \varphi''(r) = Z \Rightarrow \int_0^\infty dr\, r\, \varphi''(r) = 1$$

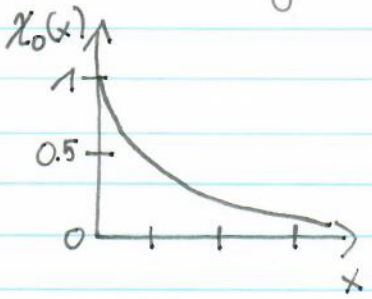
$$\left(r\,\varphi'(r)\right)\Big|_0^\infty - \int_0^\infty dr\, \varphi'(r) = \lim_{r\to\infty}\left(r\,\varphi'(r)\right) - \lim_{r\to\infty}\varphi(r) + 1 = 1$$

$$\Rightarrow \varphi'(\infty) = \varphi(\infty) = 0 \Leftrightarrow \chi'(\infty) = \chi(\infty) = 0$$

$$\chi''(x) = \frac{\chi(x)^{3/2}}{\sqrt{x}}, \quad \chi(0) = 1, \quad \chi(\infty) = 0 \quad (33)$$

$\Rightarrow$ Solution $\chi_0(x)$ (numerically)

Effective potential: $V(\vec{r}) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\chi_0\left(\frac{r}{b_0}\right)$, $b_0 = a_0\left(\frac{3\pi}{8\cdot 12}\right)^{2/3}$



⇒ Potential $-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$ of the atomic nucleus is screened by the electron cloud

⇒ Screening length scale $b_0 \sim a_0\left(\frac{1}{Z}\right)^{1/3}$

Remark: Solution of Eq. (30):

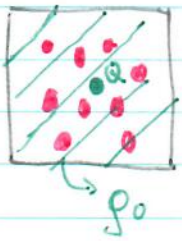
⇒ Particular solution which fulfills boundary conditions at $x = \infty$ ($\chi(\infty) = 0$):

$\chi(x) = \frac{144}{x^3}$ ⇒ violates boundary condition $\chi(0) = 1$

⇒ Semianalytical approximate solution by Majorana (Am. J. Phys. 70, 852)

⇒ Exact analytical solution not possible ⇒ Numerical solution

(a) Jellium model: ⊙ negative charge of the electrons is compensated by positive background charge: $\rho_0 = en$



⊙ System is in equilibrium: $E_0 = \varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$ does not change when additional charge Q is put into the system!

⇒ Under these conditions, Eq. (24) becomes:

$$\Delta V(\vec{r}) = -\frac{1}{3\pi^2}\frac{e^2}{\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} - V(\vec{r})\right)^{3/2} + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r}) + \frac{e^2 n}{\varepsilon_0}$$

$$= -\frac{e^2 n}{\varepsilon_0}\left[1 - \frac{V(\vec{r})}{\varepsilon_F}\right]^{3/2} + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r}) + \frac{e^2 n}{\varepsilon_0} \quad (31)$$

⇒ Expand $\left[1 - \frac{V(\vec{r})}{\varepsilon_F}\right]^{3/2}$ for small values of the perturbation $\frac{V(\vec{r})}{\varepsilon_F}$:

$$\left[1 - \frac{V(\vec{r})}{\varepsilon_F}\right]^{3/2} = 1 - \frac{3}{2}\frac{V(\vec{r})}{\varepsilon_F} + O\left(\left(\frac{V(\vec{r})}{\varepsilon_F}\right)^2\right) \quad (32)$$

$$\Delta V(\vec{r}) = -\frac{e^2 n}{\varepsilon_0} + \frac{3e^2 n}{2\varepsilon_0 \varepsilon_F} V(\vec{r}) + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r}) + \frac{e^2 n}{\varepsilon_0}$$

$$\frac{3e^2}{2\varepsilon_0 \varepsilon_F} n = \frac{3}{2}\frac{e^2}{\varepsilon_0}\frac{2m}{\hbar^2}(3\pi^2 n)^{-2/3} \cdot n = \frac{12\pi}{(3\pi^2)^{2/3}}\frac{n^{1/3}}{a_0} = \boxed{4\left(\frac{3}{\pi}\right)^{1/3}\frac{n^{1/3}}{a_0} = \frac{1}{\lambda_{TF}^2}} \quad (33)$$

λ_{TF} ... Thomas Fermi screening length $\qquad \boxed{\lambda_{TF} = \frac{1}{2}\left(\frac{\pi}{3}\right)^{1/6}\cdot\sqrt{a_0 n^{-1/3}}} \quad (34)$

(~ geometrical mean of Bohr radius a_0 and average distance between the electrons $n^{-1/3}$)

$\Rightarrow$ Ansatz: $V(\vec{r}) = -\frac{eQ}{4\pi\varepsilon_0}\frac{1}{r}\varphi(r)$ (Spherical symmetry has been assumed: $V(\vec{r}) = V(|\vec{r}|) = V(r)$)

$$\Rightarrow \Delta V(\vec{r}) = -\frac{eQ}{4\pi\varepsilon_0}\Big[\underbrace{\left(\Delta\frac{1}{r}\right)}_{-4\pi\delta^{(3)}(\vec{r})}\varphi(r) + \left(\vec{\nabla}\frac{1}{r}\right)\left(\vec{\nabla}\varphi(r)\right) + \frac{1}{r}\Delta\varphi(r)\Big]$$

$$= \frac{eQ}{\varepsilon_0}\underbrace{\delta^{(3)}(\vec{r})\cdot\varphi(r)}_{\delta^{(3)}(\vec{r})\varphi(0)} + \left[2\underbrace{\frac{\vec{r}}{r^3}\frac{\vec{r}}{r}}_{\frac{1}{r^2}}\frac{\partial\varphi}{\partial r}(r) - \frac{1}{r}\left(\frac{\partial^2\varphi}{\partial r^2}(r) + \frac{2}{r}\frac{\partial\varphi}{\partial r}(r)\right)\right]\frac{eQ}{4\pi\varepsilon_0} \quad (35)$$

$$\Delta V(\vec{r}) = \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r})\,\varphi(0) - \frac{eQ}{4\pi\varepsilon_0}\frac{1}{r}\varphi''(r) = -\frac{1}{\lambda_{TF}^2}\frac{eQ}{4\pi\varepsilon_0}\frac{1}{r}\varphi(r) + \frac{eQ}{\varepsilon_0}\delta^{(3)}(\vec{r})$$

↳ Boundary condition: $\varphi(0) = 1$

$$\Rightarrow \quad \boxed{\varphi''(r) = \frac{1}{\lambda_{TF}^2}\varphi(r)\,, \quad \varphi(0)=1\,, \quad \varphi(\infty)=0} \qquad (36)$$

$$\Rightarrow \quad \varphi(r) = e^{-\frac{r}{\lambda_{TF}}} \quad \Rightarrow \quad \boxed{V(\vec{r}) = -\frac{eQ}{4\pi\varepsilon_0}\frac{e^{-\frac{r}{\lambda_{TF}}}}{r}} \qquad (37) \ldots \text{Yukawa Potential}$$

Question: How many electrons participate in the screening:

$$\text{Average number } N_{SCREEN} = \lambda_{TF}^3 \cdot n = \frac{1}{8}\sqrt{\frac{\pi}{3}}\sqrt{a_0^3 n} \qquad (38)$$

$\Rightarrow$ If the average distance between the electrons ($\sim n^{-1/3}$) is of the order of the Bohr radius a_0 $\Rightarrow$ $a_0^3 n \sim 1$:

$\Rightarrow$ $\boxed{N_{SCREEN} = O(1)}$ $\rightarrow$ on average only one electron contributes to screening and to the effective potential $V(\vec{r})$!

$\Rightarrow$ In principle mean field theory is not fully justified!

⊙ Hartree-Fock Theory:

$N = Z$ electrons in an atom: $H = \sum_{i=1}^{N} H_0^{(i)} + \sum_{i<j=1}^{N} V^{(ij)}$ (39)

($H_0^{(i)}$: acts in Hilbert space of particle i! $V^{(ij)}$: acts in Hilbert spaces of particles i & j!; H_0: H_0; H_I: H_I (see Eq. (5))

Ansatz: Ground state of H can be approximated by Slater determinant!

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} (-1)^{\pi} |\varphi_{\pi(1)}\rangle_{(1)} \otimes \dots \otimes |\varphi_{\pi(N)}\rangle_{(N)} \quad (40)$$

Goal: Find „optimal" single-particle states $|\varphi_1\rangle \dots |\varphi_N\rangle$!

⇒ 2 criteria should be fulfilled:

→ $E_0 = \langle\psi|H|\psi\rangle \Rightarrow$ Minimal: $E_0 = \min_{|\varphi_i\rangle} \langle\psi|H|\psi\rangle$ (41)

→ Single particle states should be orthonormal: $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$

⇒ Extreme value problem under constraints:

$$\min_{|\varphi_i\rangle} \Big[\underbrace{\langle\psi|H|\psi\rangle}_{E_0} - \sum_{i,j=1}^{N} \varepsilon_{ij} \langle\varphi_i|\varphi_j\rangle \Big] \qquad (4.2)$$

ε_{ij} ↳ Lagrange Multipliers

For $|\psi\rangle$ given by a Slater determinant [see Eq. (4.0)] we have:

$$\langle\psi|H|\psi\rangle = \sum_{i=1}^{N} \langle\varphi_i|H_0|\varphi_i\rangle + \sum_{i<j=1}^{N} \langle\varphi_i|\otimes\langle\varphi_j|V|\varphi_j\rangle\otimes|\varphi_i\rangle - \langle\varphi_i|\otimes\langle\varphi_j|V|\varphi_i\rangle|\varphi_j\rangle \qquad (4.3)$$

(Exchange Term)

↳ Sum over all occupied single particle states!

$\langle\varphi_i|\otimes\langle\varphi_j|\, V\, |\varphi_k\rangle\otimes|\varphi_e\rangle$

$\langle\varphi_i|$: Hilbert space of 2nd particle; $|\varphi_k\rangle$: Hilbert space of 1st particle; $|\varphi_e\rangle$: Hilbert space of 2nd particle

e.g.: $V = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}^{(1)} - \vec{r}^{(2)}|}$

$\vec{r}^{(1)}$ ... acts in Hilbert space of 1st particle

$\vec{r}^{(2)}$ ... acts in Hilbert space of 2nd particle

⇒ in position-spin eigenbasis $|\vec{r}\,\sigma\rangle$:

$$\langle\vec{r}_2\sigma_2|\otimes\langle\vec{r}_1\sigma_1|\, V\, |\vec{r}_1'\sigma_1'\rangle\otimes|\vec{r}_2'\sigma_2'\rangle = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \delta_{\sigma_1\sigma_1'} \times \qquad (4.4)$$

$$\times\, \delta_{\sigma_2\sigma_2'}\, \delta_{\vec{r}_1\vec{r}_1'}\, \delta_{\vec{r}_2\vec{r}_2'}$$

Minimization:

$$\frac{\delta}{\delta\langle\varphi_k|}\Big[\sum_{i=1}^{N}\langle\varphi_i|H_0|\varphi_i\rangle+\sum_{i,j=1}^{N}\langle\varphi_i|\langle\varphi_j|V|\varphi_j\rangle|\varphi_i\rangle-\langle\varphi_i|\langle\varphi_j|V|\varphi_i\rangle|\varphi_j\rangle - \sum_{i,j=1}^{N}\varepsilon_{ij}\left(\langle\varphi_i|\varphi_j\rangle-\delta_{ij}\right)\Big]=0 \qquad (45)$$

$$\Rightarrow \quad H_0|\varphi_k\rangle+\sum_{j\neq k=1}^{N}\langle\varphi_j|V|\varphi_j\rangle|\varphi_k\rangle-\langle\varphi_j|V|\varphi_k\rangle|\varphi_j\rangle=\underbrace{\sum_{j=1}^{N}\varepsilon_{kj}|\varphi_j\rangle} \qquad (46)$$

can be diagonalized: $\varepsilon_{kj}=\varepsilon_k\delta_{jk}$

⇒ System of coupled Schrödinger equations for the N lowest single-particle states.

⇒ For electrons in an atom [Eq. (5)]: (Density of the other electrons!)

$$\Big[-\frac{\hbar^2}{2m}\Delta-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|}\Big]\varphi_k(\vec{r})+\frac{e^2}{4\pi\varepsilon_0}\sum_{j\neq k}\int_{\mathbb{R}^3}d^3r'\,\frac{|\varphi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\varphi_k(\vec{r})-\frac{\varphi_j^*(\vec{r}\,')\varphi_k(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\varphi_j(\vec{r})=\varepsilon_k\varphi_k(\vec{r}) \qquad (47)$$

⇒ Coupled integro-differential Eqs.!

Hartree term (density) — Fock term (exchange)