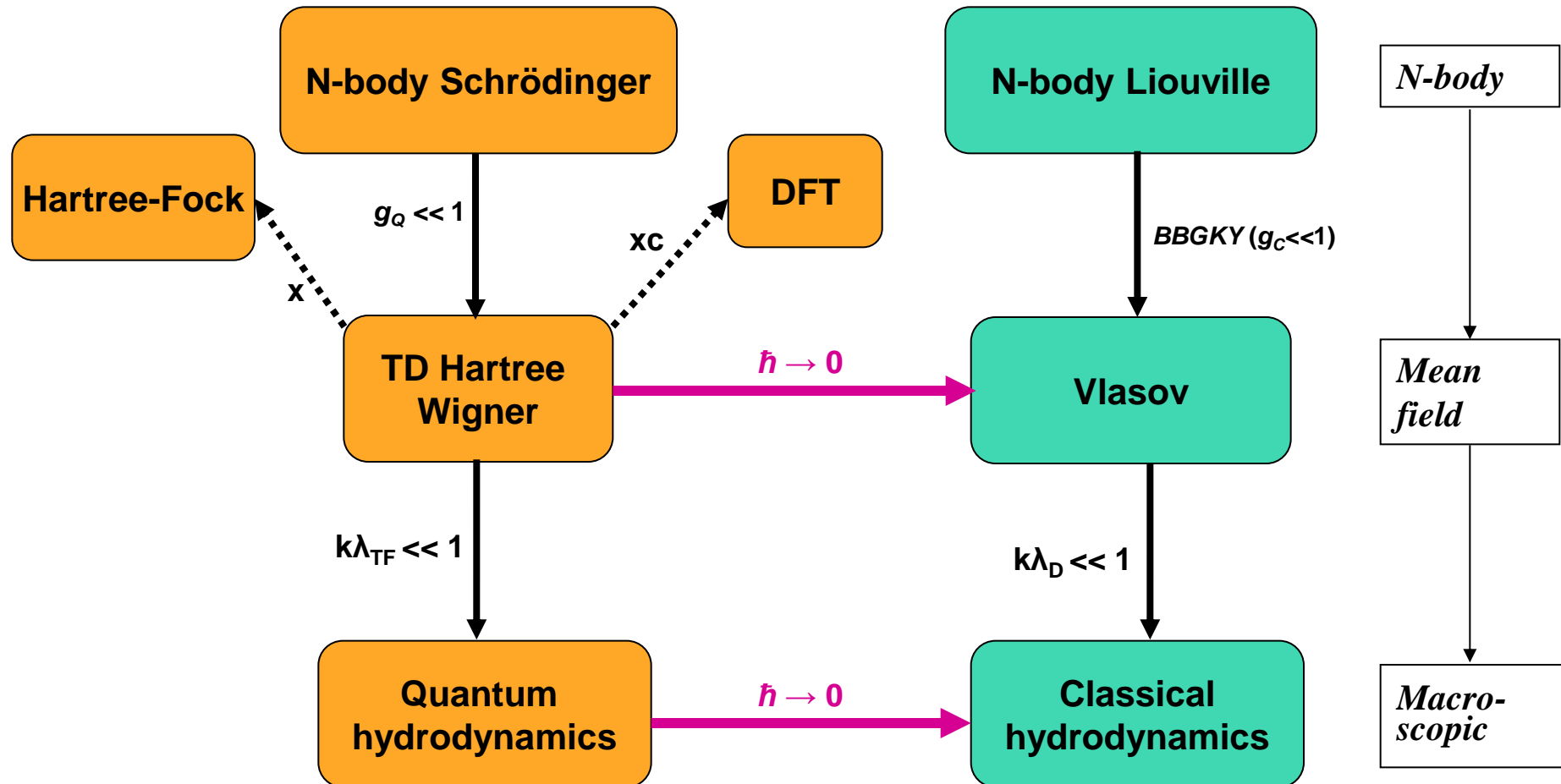


Plan of the lectures

1. Introductory remarks on metallic nanostructures
 - Relevant quantities and typical physical parameters
 - Applications
2. Linear electron response: Mie theory and generalizations
3. Nonlinear response
 - Survey of various models from N-body to macroscopic
 - Mean-field approximation (Hartree and Vlasov equations)
- 4. Beyond the mean-field approximation**
 - **Hartree-Fock equations**
 - **Time-dependent density functional theory (DFT) and local-density approximation (LDA)**
5. Macroscopic models: quantum hydrodynamics
Linear theory and comparison of various models
6. Spin dynamics: experimental results and recent theoretical advances
7. Illustration: the nonlinear electron dynamics in thin metal films

Synopsis of classical and quantum models




Beyond mean-field theory: Hartree-Fock equations

- In deriving the Hartree equations, we assumed that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) = \psi_1(\mathbf{r}_1, t) \psi_2(\mathbf{r}_2, t) \dots \psi_N(\mathbf{r}_N, t)$$

- This does not satisfy the antisymmetric property of fermions (Pauli exclusion principle):

$$\Psi(r_1, \dots, r_i, r_j, \dots, r_N) = -\Psi(r_1, \dots, r_j, r_i, \dots, r_N)$$


- Antisymmetry can be reinstated as follows (ex. for 2 particles):

$$\Psi(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) - \psi_2(r_1)\psi_1(r_2) \equiv \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) \\ \psi_2(r_1) & \psi_2(r_2) \end{vmatrix} \quad \text{“Slater determinant”}$$

- The procedure is easily generalized to N particles

Hartree-Fock equations

- Using the same variational procedure as done for the Hartree equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\mathbf{r})+V_{ext}(\mathbf{r})\psi_k(\mathbf{r})+\frac{e^2}{4\pi\epsilon}\sum_{j=1}^N\left\{\underbrace{\int d\mathbf{r}'\frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Hartree ("direct") term}}\psi_k(\mathbf{r})-\underbrace{\int d\mathbf{r}'\frac{\psi_j^*(\mathbf{r}')\psi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Fock ("exchange") term}}\psi_j(\mathbf{r})\right\}=\varepsilon_k\psi_k(\mathbf{r})$$

- NB: The exchange term is NOT in the form $V(\mathbf{r})\psi_k(\mathbf{r})$
 - Much harder to solve numerically.
- Time-dependent Hartree-Fock equations. Substitute:

$$\varepsilon_k \rightarrow i\hbar\frac{\partial}{\partial t}$$

Solution of stationary HF equations

- Only possible in special cases:
 - Uniform ionic density ($n_i = n_e = \text{const.}$)
 - Hartree potential exactly cancels ionic (“external”) potential

$$\Delta V_H + \Delta V_{ion} = \frac{e}{\varepsilon} (n_e - n_i) = 0$$

- Only **exchange** and **kinetic energy** terms survive
- Choose wave functions as **plane waves**:

$$\psi_i(r) = \frac{e^{ik_i \cdot r}}{\sqrt{V}}$$

Hartree-Fock

In this cas, the Hartree-Fock equations can be written as (see Ashcroft and Mermin):

$$H \psi_i = \epsilon(\vec{k}_i) \psi_i$$

The total energy E is:

$$E = \sum_{\vec{k} < k_F} \epsilon(\vec{k}) = V \int \frac{d\vec{k}}{(2\pi)^3} \epsilon(\vec{k}) \quad (\text{transform summation into integral})$$

$$E = N \left(\underbrace{\frac{3}{5} E_F}_{E_{\text{kin}}} - \underbrace{\frac{3}{4} \frac{e^2 k_F}{4\pi^2 \epsilon_0}}_{E_X} \right)$$

$$E_X \sim n^{1/3}$$

$$\frac{E_X}{E_F} \sim \frac{r_s}{a_0} = O(1) \text{ in metals } \approx g_Q$$

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$E = E_{\text{kin}} + E_X + E_H + E_{\text{ext}} + E_C$$

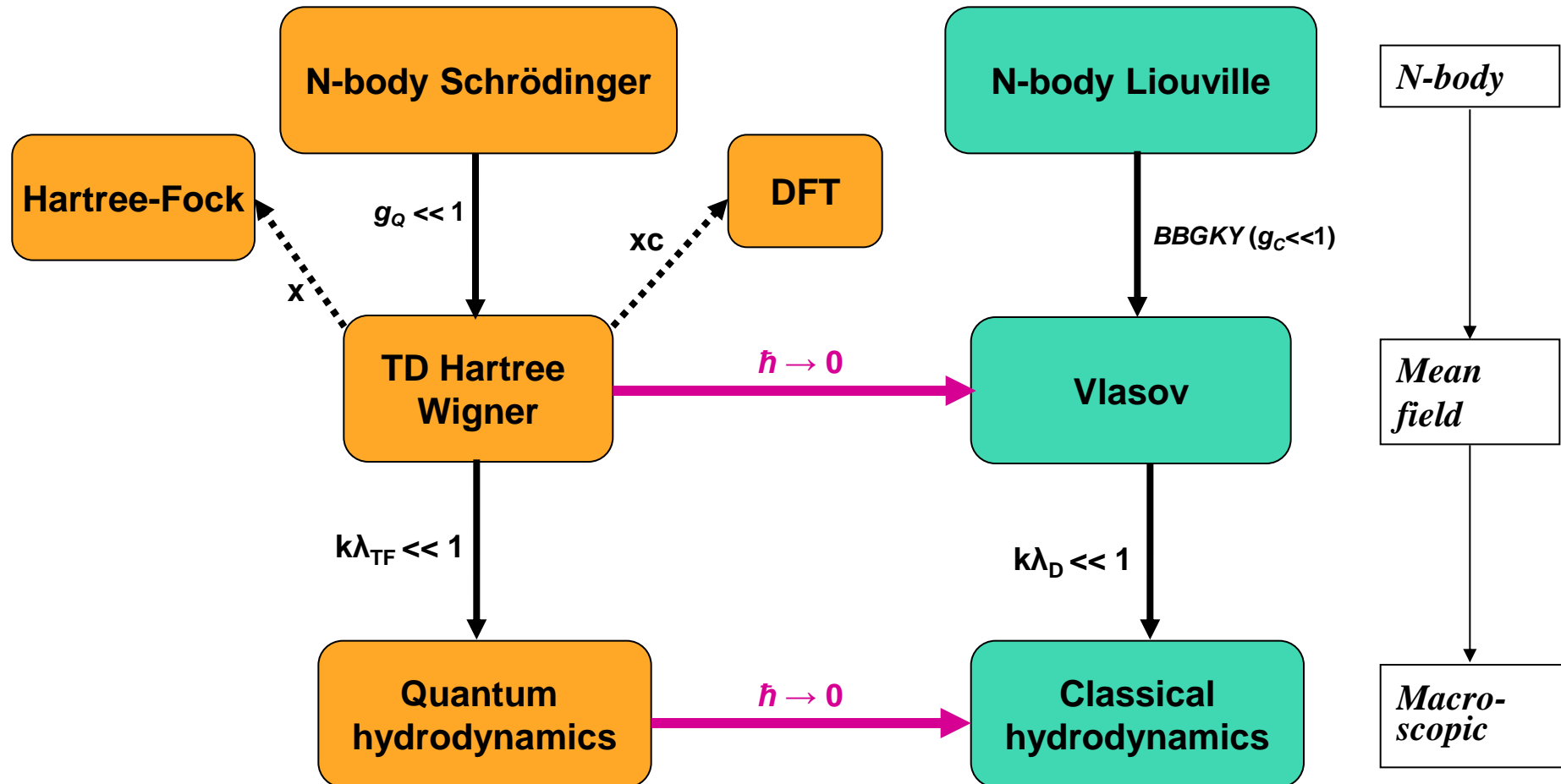
E_C = "correlation energy"

It contains all other terms beyond Hartree-Fock

Hartree-Fock: summary

- **Hartree equations** imply factoring the N-body wave function (*mean field theory*)
 - Neglect two-body correlations
 - Does not satisfy Pauli exclusion principle
- **Hartree-Fock (HF) equations** satisfies Pauli's exclusion principle
- **HF contains an additional “exchange” term**
 - Difficult to compute in practice (e.g., numerically)
- **HF can be solved exactly in a homogeneous system**
 - Use plane waves as basis
- **Obtain additional exchange energy: $E_X \sim k_F \sim n^{1/3}$**
 - Valid only for $n = \text{const.}$ (homogeneous density)
 - Question: possible to generalize to inhomogeneous density?
- **Other terms beyond E_X are called “correlation energy” (not included in HF)**
 - NB: strictly speaking, the exchange energy is also a correlation energy

Synopsis of classical and quantum models



Beyond the mean field – Density functional theory (DFT)

- In Hartree-Fock theory, in the homogeneous-density case, the exchange energy is a function of the particle density: $E_X(n) \sim n^{1/3}$
- (NB: the Hartree energy is also a function of the density)
- This is an exact result for the homogeneous case.

Two questions:

1. Is it possible to generalize the expression for $E_X(n)$ to inhomogeneous densities $n(r)$?
2. Can one also express the correlation energy as a functional of the density?

$$E = E_{\text{kin}} + E_X + E_H + E_{\text{ext}} + E_C$$

The answer is YES, and the theory behind it is called “density-functional theory”, or DFT.

Basics of DFT — Hohenberg-Kohn theorem

Walter Kohn
Nobel Prize for Chemistry, 1998



“The ground state density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely.”

$v(r) \Rightarrow n(r)$: trivial

$n(r) \Rightarrow v(r)$: ???

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Inhomogeneous Electron Gas*

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(Received 18 June 1964)

First Hohenberg-Kohn theorem (1964)

$n(r)$ = ground-state density ; $v_{1,2}(r)$ = external potentials

$$H_1 = v_1 + T + U$$

T = kinetic energy : U = e-e interaction energy

Let $n(r)$ be the non-degenerate ground-state density of N electrons in the potential v_1 , corresponding to the wavefunction Ψ_1 and the energy E_1 . Then:

$$\begin{aligned} E_1 &= (\Psi_1, H_1 \Psi_1) \\ &= \int v_1(r) n(r) dr + (\Psi_1, (T + U) \Psi_1), \end{aligned}$$

Now suppose that there exists a second potential $v_2 \neq v_1$ with ground state $\Psi_2 \neq \Psi_1$ giving rise to the same density $n(r)$. Then:

$$E_2 = \int v_2(r) n(r) dr + \int (\Psi_2, (T + U) \Psi_2).$$

In virtue of the variational principle, one has:

$$\begin{aligned} E_1 &< (\Psi_2, H_1 \Psi_2) \\ &= \int v_1(r) n(r) dr + (\Psi_2, (T + U) \Psi_2) \\ &= E_2 + \int [v_1(r) - v_2(r)] n(r) dr. \end{aligned}$$

By exchanging the roles of 1 and 2, we obtain:

$$E_2 \leq (\Psi_1, H_2 \Psi_1) = E_1 + \int [v_2(r) - v_1(r)] n(r) dr,$$

$$E_1 + E_2 < E_1 + E_2$$

contradiction!

First Hohenberg-Kohn theorem

- Thus the hypothesis of the existence of a second potential $v_2 \neq v_1$ is wrong.
- Hence the theorem: **“The ground-state density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely.”**
- Hence, $n(r)$ determines all the properties of the system.
- This is a big step, because the wave function $\Psi(r_1, r_2, \dots, r_N)$ “lives” in a $3N$ -dimensional space, whereas the density $n(r)$ lives in a 3D space.
- Try to mesh a $3N$ -dimensional space with 10 points per direction: 10^{3N} points
- For a 3D space: 10^3 points = 8 kB

N=3	8 GB
N=4	8000 GB
N=5	8 million Gb

Each point = 8 bytes (Fortran double-precision real numbers)

Second HK theorem

- The ground-state energy can be obtained variationally: the density that minimizes the total energy is the exact ground-state density.***

$$E[n] = \int V(r)n(r)dr + T[n] + U[n]$$

e-e interactions

- The e-e interaction energy is then separated into a Hartree (mean field) contribution and an exchange-correlation contribution:

$$U[n] = E_H[n] + E_{XC}[n]$$

$$E[n] = \int V(r) n(r) dr + \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(r') n(r)}{|r-r'|} dr' dr + T[n] + E_{xc}[n]$$

external

Hartree

kinetic

exchange-
correlations

Example: Thomas-Fermi theory

$$E[n] = \int V(r) n(r) dr + \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(r') n(r)}{|r-r'|} dr' dr + T[n] + E_{xc}[n]$$

In the Thomas-Fermi approximation:

$$\begin{cases} T_{TF}[n] = \frac{3}{10} (3\pi^2)^{2/3} \frac{\hbar^2}{m} \int n^{5/3} dr ; & \delta T_{TF} = \int E_F(n) \delta n dr \\ E_{xc}[n] = 0 \end{cases}$$

Variational principle with fixed number of particles $\int n dr = N$

$$\delta \left\{ E[n] - \mu \int n dr \right\} = \int \left\{ V + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(r')}{|r-r'|} dr' + E_F(n) - \mu \right\} \delta n(r) dr = 0$$

$$V(r) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(r')}{|r-r'|} dr' + \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \mu$$

Thomas-Fermi eqs.

Thomas-Fermi theory: calculation of the kinetic energy

$$\underbrace{\frac{4\pi}{3} p_F^3}_{\text{momentum space}} \cdot \underbrace{V}_{\text{coordinate space}} \cdot \frac{2}{h^3} = N$$

$$N = \frac{\text{Phase-space volume}}{h^3} \times 2$$

$$\rho = \frac{N}{V} = \frac{8\pi}{3h^3} p_F^3 \quad p_F = \left[\frac{3h^3}{8\pi} \rho \right]^{1/3}$$

T = kinetic energy
 t = kinetic energy density
 ρ = density

$$\begin{aligned} t &= \frac{T}{V} = \frac{1}{V} \int \frac{p^2}{2m} dN_p = \frac{1}{V} \int_0^{p_F} \frac{p^2}{2m} \cdot \frac{4\pi p^2 \cdot V \cdot 2}{h^3} dp \\ &= \frac{8\pi}{2mh^3} \int_0^{p_F} p^4 dp = \frac{8\pi}{2mh^3} \cdot \frac{p_F^5}{5} \end{aligned}$$

$$T = \int t(\mathbf{r}) d\mathbf{r}.$$

$$t = \frac{8\pi}{2mh^3} \cdot \frac{1}{5} \left[\frac{3h^3}{8\pi} \rho(\mathbf{r}) \right]^{5/3} = \underbrace{\frac{3h^2}{10m} \left(\frac{3}{8\pi} \right)^{2/3}}_{C_K} [\rho(\mathbf{r})]^{5/3}$$

Kohn-Sham theory I.

$$E = \min_{\psi \rightarrow N} \langle \psi | \hat{H} | \psi \rangle ;$$

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

kinetic \downarrow e-e \downarrow external

$$= \min_{n \rightarrow N} \left\{ \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{U} | \psi \rangle + \int n V d\vec{r} \right\}$$

$$= \min_{n \rightarrow N} \left\{ T[n] + U[n] + \int n V d\vec{r} \right\}$$

$$\bullet U[n] = \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\vec{r}') n(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + E_{xc}[n]$$

$$\bullet T[n] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} | \psi \rangle$$

Fundamental equation of DFT : $\frac{\delta E}{\delta n} \equiv \frac{\delta T}{\delta n} + \frac{\delta U}{\delta n} + V - \mu = 0$

Two strategies:

1) Orbital-free DFT : $T[n]$ = function of n (and derivatives)

Ex: Thomas-Fermi : $T[n] = k \int n^{5/3} d\vec{r}$

2) Kohn-Sham approach

Kohn-Sham theory II.

KOHN-SHAM THEORY

$$\left. \begin{aligned} T[n] &= T_s[n] \\ E'_{xc} &= E_{xc} + \underbrace{(T - T_s)}_{\text{small}} \end{aligned} \right\} \text{still exact.}$$

$$E = \min_{\psi \rightarrow N} \langle \psi | \hat{H} | \psi \rangle = \min_{\psi \rightarrow N} \underbrace{\langle \psi | \hat{T} | \psi \rangle}_{\text{minimize}} + \min_{n \rightarrow N} \left\{ U[n] + \int n V dr \right\}$$

Note difference from T-F theory here

Approx ψ as product of single-particle w.f. $\psi_j(r)$, $j=1 \dots N$

$$\langle \psi | \hat{T} | \psi \rangle = \sum_j \langle \phi_j | -\frac{\hbar^2 \nabla^2}{2m} | \phi_j \rangle \Big|_{\sum_j |\phi_j|^2 = n}$$

$$\sum_j |\phi_j|^2 = n$$

Then, fundamental eq. of DFT is:

$$0 = \frac{\delta}{\delta \psi_j} \langle \phi_j | -\frac{\hbar^2 \nabla^2}{2m} | \phi_j \rangle \Big|_{\sum_j |\phi_j|^2 = n} + \underbrace{\frac{\delta E_H}{\delta n}}_{V_H} + \underbrace{\frac{\delta E_{xc}}{\delta n}}_{V_{xc}} + V - \mu$$

$$V_{\text{eff}} = V_H + V_{xc} + V$$

Kohn-Sham equations

- But this is the same variational principle for a single-particle Schrödinger equation evolving in the potential V_{eff}
- The minimum is attained for wave-function that obeys the equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Kohn-Sham equations

$$V_{eff}[n(r)] = V(r) + V_H[n] + V_{XC}[n]$$

$$V_{XC}[n] \equiv \frac{\delta E_{XC}}{\delta n}$$

$$V_H[n] \equiv \frac{\delta E_H}{\delta n}$$

- NB: if we set $V_{XC} = 0$, we recover the Hartree equations.
 - The KS equations are a formal “exactification” of the Hartree theory.

The local-density approximation (LDA)

- Approximate the exchange and correlation with a local functional
- The local-density approximation is exact for the exchange energy of a uniform electronic system
 - Plane-wave wavefunctions for the electrons
 - Uniform positive charge distribution for the ions
- For a non-uniform system, we can conjecture:

$$E_X[n] = \int \epsilon_X[n] n(r) d^3r = -\frac{3}{4} \frac{e^2}{4\pi^2 \epsilon_0} (3\pi^2)^{1/3} \int n^{4/3}(r) d^3r$$

- For the correlation energy the exact expression is not known
- But the Hohenberg-Kohn theorem tells us that such a functional **exists**
 - Various approximations have been proposed
- All in all, it works quite well, despite its simplicity

Time-dependent density functional theory (TDDFT)

- Runge and Gross, 1984:

“The densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ evolving from a common initial state $\Psi(t=0)$, under the influence of two external potentials $V_{\text{ext}}(\mathbf{r}, t)$ and $V'_{\text{ext}}(\mathbf{r}, t)$ will eventually differ only if the potentials differ by more than a purely time-dependent functions, i.e., $V_{\text{ext}}(\mathbf{r}, t) - V'_{\text{ext}}(\mathbf{r}, t) \neq c(t)$.”

- One-to-one mapping between densities and potentials
 - The potential is a *functional* of the density
- **Time-dependent Kohn-Sham equations:**

$$i\hbar \frac{\partial}{\partial t} \phi_k(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}, t) \right) \phi_k(\mathbf{r}, t)$$

$$V_{\text{eff}}[n(\mathbf{r}, t)] = V(\mathbf{r}, t) + V_H[n(\mathbf{r}, t)] + V_{XC}[n(\mathbf{r}, t)]$$

TABLE II: Top-10 cited PR articles. The asterisks denote citation undercount due to citations with missing prepended A/B page numbers – 123 out of 3227 total for item 1 and 120 out of 2640 for item 2.

Impact Rank	Publication			# cites	Av. Age	Impact	Title		Author(s)
1	PR	140	A1133	1965	3227*	26.64	85972	Self-Consistent Equations...	W. Kohn & L. J. Sham
2	PR	136	B864	1964	2460*	28.70	70604	Inhomogeneous Electron Gas	P. Hohenberg & W. Kohn
3	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to...	J. P. Perdew & A. Zunger
4	PRL	45	566	1980	1781	15.42	27463	Ground State of the Electron ...	D. M. Ceperley & B. J. Alder
5	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer
6	PRL	19	1264	1967	1306	15.46	20191	A Model of Leptons	S. Weinberg
7	PRB	12	3060	1975	1259	18.35	23103	Linear Methods in Band Theory	O. K. Andersen
8	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
8	RMP	57	287	1985	1055	9.17	9674	Disordered Electronic Systems	P. A. Lee & T. V. Ramakrishnan
9	RMP	54	437	1982	1045	10.82	11307	Electronic Properties of...	T. Ando, A. B. Fowler, & F. Stern
10	PRB	13	5188	1976	1023	20.75	21227	Special Points for Brillouin...	H. J. Monkhorst & J. D. Pack

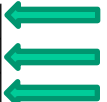


TABLE III: The top-10 PR articles ranked by citation impact.

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3	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
4	PR	40	749	1932	561	55.76	31281	On the Quantum Correction...	E. Wigner
5	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to...	J. P. Perdew & A. Zunger
6	PR	82	403	1951	643	46.35	29803	Interaction Between d-Shells ...	C. Zener
7	PR	47	777	1935	492	59.64	29343	Can Quantum-Mechanical...	A. Einstein, B. Podolsky, & N. Rosen
8	PR	46	1002	1934	557	51.49	28680	On the Interaction of...	E. Wigner
9	PR	109	1492	1958	871	32.00	27872	Absence of Diffusion in...	P. W. Anderson
10	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer



Synopsis of classical and quantum models

