Dynamics of interacting electrons

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Outline

1. Introduction to the governing equations
2. Thomas-Fermi-Maxwell model
3. Kohn-Sham model and scalings
4. Homogenized system - high frequency regime
5. Homogenized systems - low frequency regime
Many-body Schrödinger equation

In the Born-Oppenheimer approximation,

\[
i\hbar \frac{\partial \Psi}{\partial t} = H \Psi = \left(-\frac{\hbar^2}{2m_e} \Delta + V\right) \Psi,
\]

\[V = V_{ne} + V_{ee} + W.\]

\(V_{ne}\) – the electron-nucleus attraction energy
\(V_{ee}\) – the electron-electron repulsion energy
\(W\) – the external potential

\(N\) electrons \(\rightarrow\) dimensionality of equation \(3N + 1\)

Conclusion:
\textit{nice} equation but \textit{mission impossible} to be directly solved
Hartree-Fock and TDDFT theory

Hartree-Fock theory: $\Psi$ has the form of determinant $\{\psi_k\}_{k=1}^N$ – Slater determinant

\[ i\hbar \frac{\partial \psi_k}{\partial t} = -\frac{\hbar^2}{2m_e} \Delta \psi_k + V \psi_k, \]

\[ V = V_H + V_F + W. \]

$V_H$ - Hartree (Coulomb) potential
$V_F$ - Fock (exchange) operator

TDDFT theory (Runge-Gross theorem, 1984): a unique map between the time-dependent external potential and time-dependent density.

$V = V_{\text{eff}}(\rho), \rho = \sum_k |\psi_k|^2 \implies$ Thomas-Fermi system (orbital-free) and Kohn-Sham system (orbital-dependent).
Motivations

- Understand the electron interactions under the picture of Hartree-Fock or TDDFT;
- Derive effective equations in the background of crystals;
- Aim at possible applications in nano-optics and semiconductors.
Derivation of the Thomas-Fermi-Maxwell model

Begin from the quantum many-body action

\[ \mathcal{A} = \int < \Psi | i \partial_t - H | \Psi > \, dt. \]

Take \( \Psi \) as the Slater determinant \( \{ \psi_k \}_{k=1}^N \) and assume
\[ \psi_k = a_k \exp(iS) - \text{same phase function}, \]

\[ \mathcal{A} = \int \rho \left( -\partial_t S - \frac{1}{2} (A - \nabla S)^2 \right) - < \Psi | H_0 | \Psi > \, dt, \]

where \( \rho = \sum_k |a_k|^2 \) we have also considered the magnetic vector potential \( A \) in the Hamiltonian

\[ H = \frac{1}{2} (i\nabla + A)^2 + V, \quad H_0 = -\frac{1}{2} \Delta + V. \]
Euler-Lagrange equations

The Thomas-Fermi approximation of kinetic energy yields,

\[ A = \int \rho \left(-\partial_t S - \frac{1}{2} (A - \nabla S)^2\right) - C_{TF} \rho^{5/3} - \rho V_c - \epsilon_{xc}(\rho) \, dt. \]

The Euler-Lagrange equations read as

\[ \partial_t \rho + \nabla \cdot (\rho (\nabla S - A)) = 0, \]
\[ \partial_t S + \frac{1}{2} (\nabla S - A)^2 + \frac{\delta E_{TF}}{\delta \rho} = 0, \]
\[ E_{TF} = C_{TF} \int \rho^{5/3} + \int \rho V_c + \int \epsilon_{xc}(\rho), \]

coupled with the Maxwell system

\[ \partial_t^2 A - \Delta A + \nabla(\partial_t V_c) = J = \rho (\nabla S - A), \]
\[ - \Delta V_c = \rho - m, \quad m \text{ – nuclei charge}. \]
Linearized half space problem
(Ritchie, 1973, dispersion of surface plasmon)

G.S. \[ \rho_0(x, z) = 1_{z > 0}, \quad A = 0, \quad V_c = 0, \quad \nabla S = 0, \]

Pert. \[ E = -\nabla \tilde{V}_c - \frac{\partial \tilde{A}}{\partial t}, \quad B = \nabla \times \tilde{A}, \]

\[ E = (E_1(z), 0, E_3(z)) e^{i(kx - \omega t)}, \quad B = (0, B_2(z), 0) e^{i(kx - \omega t)}. \]

Interface condition: \( E, \ B \) are continuous.
Dispersion relation $\omega \sim ? k$

In Drude model electron has classical dynamics

$$\frac{dp}{dt} = -\frac{p}{\tau} - E, \quad J = \rho_0 p.$$
Discussions on Thomas-Fermi-Maxwell model

- Both Drude and Thomas-Fermi models lie in the linear regime when the wave number $k$ is small (long waves).

- Out of the linear response regime, Drude model only performs well for a certain range of wave number; as $k \to \infty$ (short waves), one needs to capture the many body effects, for example, by Thomas-Fermi model.

- The nonlinear Thomas-Fermi-Maxwell model could be used to study the optical response of surface plasmon polaritons. (W. Cai and his collaborators)
Kohn-Sham model

\[ i \frac{\partial \psi_j}{\partial t} = -\frac{1}{2} \Delta \psi_j + V_{\text{eff}} \psi_j, \]

\[ V_{\text{eff}} = V_c + W + V_{xc}(\rho), \]

\[ -\Delta V_c = \rho - m, \quad \rho = \sum_j |\psi_j|^2 \text{ (spin degeneracy omitted).} \]

\( \psi_j \) - the wave function for the \( j \)-th independent electron;

\( V_{\text{eff}} \) - the effective potential; \( W \) - the external potential;

\( V_{xc} \) - the exchange-correlation potential (with adiabatic local density approximation).

\( N \) electrons \( \rightarrow \) \( N \) one body Schrödinger equation.

Goal:

Effective equations modeling electron dynamics in crystals under macroscopic perturbations.
Nondimensionalization - rescalings

We rescale the system according to the time and length scales of the external potential $W$.

The length scale $L \gg 1$, and we denote $\varepsilon = 1/L$.

The time scale $T$ distinguishes two regimes

- High frequency: $T = O(1)$.
- Low frequency: $T = O(1/\varepsilon)$;

The rescaled Schrödinger equations are given by

\[
\begin{align*}
    i\partial_t \psi_j^\varepsilon &= -\frac{1}{2} \varepsilon^2 \Delta \psi_j^\varepsilon + V(x) \psi_j^\varepsilon + W(x, t) \psi_j^\varepsilon \quad \text{(High frequency)}; \\
    i\varepsilon \partial_t \psi_j^\varepsilon &= -\frac{1}{2} \varepsilon^2 \Delta \psi_j^\varepsilon + V(x) \psi_j^\varepsilon + W(x, t) \psi_j^\varepsilon \quad \text{(Low frequency)},
\end{align*}
\]

where $V = V_c + V_{xc}$. 
Crystals - periodicity assumptions

- Assume the external potential $W$ is 1-periodic in $x$.
- The unit cell is $\varepsilon$-periodic and contains $N$ electron.

Then

$$-\varepsilon^2 \Delta V_c = \varepsilon^3 (\rho^\varepsilon - m^\varepsilon), \quad V_{xc} = \eta(\varepsilon^3 \rho^\varepsilon),$$

where

$$\rho^\varepsilon = \sum_{j=1}^{Z\varepsilon^{-3}} |\psi_j^\varepsilon|^2, \quad m^\varepsilon = \varepsilon^{-3} m(x/\varepsilon).$$
High frequency regime - short time dynamics

\[
\begin{align*}
    i \partial_t \psi_j^\varepsilon &= -\frac{1}{2} \varepsilon^2 \Delta \psi_j^\varepsilon + V(x, t) \psi_j^\varepsilon + W(x, t) \psi_j^\varepsilon, \\
    -\varepsilon^2 \Delta V_c &= \varepsilon^3 (\rho^\varepsilon - m^\varepsilon), \quad V_{xc} = \eta(\varepsilon^3 \rho).
\end{align*}
\]

Denote \( V_{tot} = V + W \).

Remark that \( \rho^\varepsilon = \sum Z \varepsilon^{-3} |\psi_j^\varepsilon|^2 \sim O(1/\varepsilon^3) \).

Assume initially the system is at the ground state \( \rho^\varepsilon(x, 0) = \varepsilon^{-3} \rho_0(x/\varepsilon) \) of the unperturbed system (\( W = 0 \)).

Interested in: macroscopic response in \( V \) to \( W \) as \( \varepsilon \to 0 \).
Band structure

Denote the Hamiltonian for the unperturbed system (in a.u.)

\[
H_0 = -\frac{1}{2}\Delta + V_{\text{per}} \quad \text{with} \quad -\Delta V_{\text{per}} = \rho_0 - m.
\]

Bloch-Floquet theory shows

\[
H_0 = \int_{\Gamma^*} H_{0,k} \, dk = \int_{\Gamma^*} \sum_n E_n(k) |\psi_{n,k}\rangle \langle \psi_{n,k}| \, dk.
\]

\(\psi_{n,k}\) and \(E_n(k)\) are the eigenfunctions and eigenvalues (sorted in increasing order) of \(H_{0,k}\). \(\psi_{n,k} = u_{n,k} \exp(i k \cdot x)\).

Band gap assumption:
The first \(Z\) bands are occupied with a gap from the others.
Main results

\[ V_{tot}(t, x) = (V_{per}(x/\varepsilon) + U_0(t, x)) + O(\varepsilon), \]

where \( U_0 \) satisfies,

\[ -\Delta_x U_0(t, x) - \int_0^t G(t - \tau) : \nabla_x^2 U_0 \, d\tau = -\Delta_x W(t, x), \]

and

\[ G(t) = \frac{1}{2\pi} \int e^{-i\omega t} G(\omega) \, d\omega. \]

A physically more clear form:

\[ -\Delta_x \hat{U}_0(\omega, x) - G(\omega) : \nabla_x^2 \hat{U}_0(\omega, x) = -\Delta_x \hat{W}(\omega, x). \]
G(\omega) is determined by the band structure

\[ G_{\alpha\beta}(\omega) = \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \text{Re} \frac{\langle u_{n,k} | i\partial_{k\alpha} | u_{m,k} \rangle \langle u_{n,k} | i\partial_{k\beta} | u_{m,k} \rangle}{\omega + \omega_{mn}(k)} \, dk \]

\[ - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \text{Re} \frac{\langle u_{n,k} | i\partial_{k\alpha} | u_{m,k} \rangle \langle u_{n,k} | i\partial_{k\beta} | u_{m,k} \rangle}{\omega - \omega_{mn}(k)} \, dk \]

\[ - \left\langle f_{\omega,\alpha}, \mathcal{V}(1 - \chi_{\omega} \mathcal{V})^{-1} f_{\omega,\beta} \right\rangle, \]

\[ \omega_{mn} = E_m(k) - E_n(k). \]
The function $f$ and operator $\chi_\omega$ from $\delta V$ to $\delta \rho$,

$$f_{\omega,\alpha} = - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{u_{n,k} u_{m,k}^*}{\omega + \omega_{mn}(k)} \langle u_{n,k} | i \partial_{k\alpha} | u_{m,k} \rangle \, dk$$

$$+ \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{u_{n,k}^* u_{m,k}}{\omega - \omega_{mn}(k)} \langle u_{n,k} | i \partial_{k\alpha} | u_{m,k} \rangle \, dk,$$

$$\chi_\omega g = - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{u_{n,k} u_{m,k}^*}{\omega + \omega_{mn}(k)} \langle u_{n,k} | g | u_{m,k} \rangle \, dk$$

$$+ \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{u_{n,k}^* u_{m,k}}{\omega - \omega_{mn}(k)} \langle u_{n,k} | g | u_{m,k} \rangle \, dk.$$

The linear map from $\delta \rho$ to $\delta V$,

$$\nabla h = \phi + \eta'(\rho_{\text{per}}) h,$$

$$- \Delta_z \phi = h.$$
Discussions on short time dynamics

- Microscopic justification of the effective Poisson equation in crystals (semiconductors or insulators).

- The external could be viewed as generated by free charge $-\Delta W$, then $\mathcal{E} = I + G$ gives the dielectric response (permittivity) tensor.

- The limit of $\omega \to 0$ recovers the static dielectric response (Baroni-Resta, 1986), recently rigorously studied by Cancés-Lewin (2010) in the linear response regime.
Asymptotics

\[
\rho = \varepsilon^{-3} \rho_0(t, x, x/\varepsilon) + \varepsilon^{-2} \rho_1(t, x, x/\varepsilon) + \varepsilon^{-1} \rho_2(t, x, x/\varepsilon) + \cdots
\]

\[
V_{\text{tot}}(t, x) = V_0(t, x, x/\varepsilon) + \varepsilon V_1(t, x, x/\varepsilon) + \varepsilon^2 V_2(t, x, x/\varepsilon) + \cdots
\]

Solvability condition:

\[
\langle \rho_0 \rangle = \langle m \rangle, \quad \langle \rho_1 \rangle = 0, \quad -\Delta_x \langle V_0 \rangle = \langle \rho_2 \rangle.
\]
Heisenberg's picture:

\[
\mathcal{P}_t^\varepsilon = \mathcal{I} \exp\left(-i \int_0^t H^\varepsilon(\tau)\right) \mathcal{P}_0^\varepsilon \left( \mathcal{I} \exp\left(-i \int_0^t H^\varepsilon(\tau)\right) \right)^*,
\]

\[
\rho^\varepsilon(t, x) = \mathcal{P}_t^\varepsilon(x, x),
\]

**Key observation:**

The domain of dependence and influence in the evolution is of scale of cell size \(\mathcal{O}(\varepsilon)\).
\[ \mathcal{H}_0(t, x) = -\frac{\varepsilon^2}{2} \Delta y + V_0(t, x, y/\varepsilon), \]
\[ \delta \mathcal{H}_1^\varepsilon(t, x) = (y - x) \cdot \nabla_x V_0(t, x, y/\varepsilon) + \varepsilon V_1(t, x, y/\varepsilon), \]
\[ \delta \mathcal{H}_2^\varepsilon(t, x) = \frac{1}{2} ((y - x) \cdot \nabla_x)^2 V_0(t, x, y/\varepsilon) \]
\[ + \varepsilon (y - x) \cdot \nabla_x V_1(t, x, y/\varepsilon) + \varepsilon^2 V_2(t, x, y/\varepsilon). \]

\[ T \exp(-i \int_0^t \mathcal{H}^\varepsilon(\tau)) \]
\[ = U_{t,0}(x_0) - i \int_0^t U_{t,\tau}(x_0) \delta \mathcal{H}^\varepsilon(\tau, x_0) U_{\tau,0}(x_0) \, d\tau \]
\[ - \int_0^t \int_0^{\tau_2} U_{t,\tau_2}(x_0) \delta \mathcal{H}^\varepsilon(\tau_2, x_0) U_{\tau_2,\tau_1}(x_0) \]
\[ \times \delta \mathcal{H}^\varepsilon(\tau_1, x_0) U_{\tau_1,0}(x_0) \, d\tau_1 \, d\tau_2 + \cdots, \]
\[ U_{t,s}(x_0) = T \exp(-i \int_s^t \mathcal{H}_0(\tau, x_0) \, d\tau). \]
Low frequency regime - long time dynamics

\[
\begin{cases}
    i\varepsilon \partial_t \psi_j^\varepsilon = -\frac{1}{2} \varepsilon^2 \Delta \psi_j^\varepsilon + V(x) \psi_j^\varepsilon + W(x, t) \psi_j^\varepsilon, \\
    -\varepsilon^2 \Delta V = \varepsilon^3 (\rho^\varepsilon - m^\varepsilon).
\end{cases}
\]

Simplifications:

- No exchange correlation potential;
- Assume we only have valance and conduction bands;
- Initially the system is at the ground state of the unperturbed system ($W = 0$).

Interested in: derivation of mesoscopic transport equations.
Two species transport equations

\[
\begin{aligned}
\text{Homogenized system:} & \\
\partial f_{1,k}^{\nu,c} + \nabla_k E_{\nu,c} \cdot \nabla_x f_{1,k}^{\nu,c} &= \mathcal{K}_{\nu,c} : \nabla_x q_{1,k}^{\nu,c} + h_{\nu,c}(\nabla_x v_1), \\
\partial_t q_{1,k}^{\nu,c} + \nabla_k E_{\nu,c} \cdot \nabla_x q_{1,k}^{\nu,c} + \nabla_x (v_1 + \langle V_1 \rangle) &= 0,
\end{aligned}
\]

\[
\text{cell problem:} \quad (-\Delta z + \mathcal{R}) v_1 = \int_{\Gamma^*} (f_{1,k}^{\nu} |\chi_\nu|^2 + f_{1,k}^{c} |\chi_c|^2) + g^{\nu} + g^{c} \, dk.
\]

Incompressibility condition: \( \langle \rho_1 \rangle = \int f_{1,k}^{\nu} + f_{1,k}^{c} \, dk = 0. \)

- For each species, we have equations for the density \( f_{1,k}^{\nu,c} \) and current \( q_{1,k}^{\nu,c} \), interacted by \( \mathcal{K}_{\nu,c} \) (given later).
- The interaction of these two species is through the microscopic potential \( v_1 \).
Discussions on long time dynamics

- $\langle V_1 \rangle$ serves as the Lagrangian multiplier.
- The closure strategy is different from the short time dynamics. The response macroscopic potential serves as the Lagrange multiplier.
- Why interested in the first order system? The number density is of order $\varepsilon^{-2}$. If we try to recover the physical system and take $\varepsilon = 10^{-10}$, then the total charge density is roughly of $\mathcal{O}(1)$.
- If the initial conditions are zero, the system has (trivial) solutions (zero). This is consistent with the fact that a pure insulator does not conduct electricity. To make a semiconductor, we need to disturb the system so that the initial conditions of the first order system are nonzero. For example, p-n junction.
\[ \psi_k = \varepsilon^{-3/2} \psi_{0,k}(t, x, x/\varepsilon) + \varepsilon^{-1/2} \psi_{1,k}(t, x, x/\varepsilon) \]
\[ + \varepsilon^{1/2} \psi_{2,k}(t, x, x/\varepsilon) + \cdots \]
\[ V(t, x) = V_0(t, x, x/\varepsilon) + \varepsilon V_1(t, x, x/\varepsilon) \]
\[ + \varepsilon^2 V_2(t, x, x/\varepsilon) + \cdots \]

Two scaled Coulomb equation, \( z = x/\varepsilon \),

\[-\Delta_z V_\ell - 2 \nabla_x \cdot \nabla_z V_{\ell-1} - \Delta_x V_{\ell-2} = \rho_\ell - \delta_{0\ell} m. \]

Constraints:

\[ \langle \rho_0 \rangle = \langle m \rangle, \quad \langle \rho_1 \rangle = 0, \quad -\Delta_x \langle V_0 \rangle = \langle \rho_2 \rangle. \]
WKB analysis

\[ \psi_{0,k}(t, x, z) = \varphi_{0,k}(t, x, z) \exp(iS_k(t, x)/\varepsilon). \]

Adiabatic approx.  \[ \varphi_{0,k}(t, x, z) = a_{0,k}(t, x) \chi_n(\nabla_x S_k, z). \]

\[ \mathcal{H}\chi_n = \left( \frac{1}{2} (-i\nabla_z + p)^2 + V_{\text{per}}(z) \right) \chi_n(p, z) = E_n(p)\chi_n(p, z). \]

Valence band:  \[ a_{0,k}^v(t, x) = 1, S_k^v(0, x) = kx \] (full band)

Conduction band:  \[ a_{0,k}^c(t, x) = 0, S_k^c(0, x) = kx \] (empty band)
To the leading order, one gets eikonal-transport equations,

\[
\begin{align*}
\partial_t S_k^{v,c} + E_{v,c}(\nabla_x S_k^{v,c}) &= 0 \quad (\Rightarrow) \quad S_k^{v,c}(t, x) = kx - E_{v,c}(k)t, \\
\partial_t a_{0,k}^{v,c} + \nabla_k E_{v,c}(k) \cdot \nabla_x a_{0,k}^{v,c} + ia_{0,k}^{v,c}(v_1 + \langle V_1 \rangle) &= 0,
\end{align*}
\]

\[
|a_{0,k}^v|^2 = 1, \quad |a_{0,k}^c|^2 = 0,
\]

\[
\langle \rho_0 \rangle = \int |a_{0,k}^v|^2 + |a_{0,k}^c|^2 \, dk = \langle m \rangle.
\]

This fulfills the behavior of insulator: although each electron has classical dynamics

\[
\frac{dX}{dt} = \nabla_k E_{v,c},
\]

it does not conduct electricity. It proposes a constraint

\[
\langle V_0 \rangle + W = 0, \quad \langle \rho_2 \rangle = \Delta_x W
\]
The first order correction. Assume

\[ \psi_{1,k}^{v,c}(t, x, z) = a_{1,k}^{v,c} \chi_{v,c}(k, z) + (\varphi_{1,k}^{v,c})^\perp. \]

Define

\[ f_{1,k}^{v,c} = 2 \Re \langle (\psi_{0,k}^{v,c})^* \psi_{1,k}^{v,c} \rangle, \quad q_{1,k}^{v,c} = \Im \langle (\psi_{0,k}^{v,c})^* \nabla_x \psi_{0,k}^{v,c} \rangle. \]

then

\[ K_{\alpha\beta}^{v,c} = 2 \Re \langle \partial_z^{\alpha} \chi_{v,c}, L_{v,c}^{-1} (I - P_{v,c}) \partial_z^{\beta} \chi_{v,c} \rangle - \delta_{\alpha\beta}, \]

\[ L_{v,c} = \mathcal{H} - E_{v,c}, \]

\[ h_{v,c}^{v,c}(\nabla_x v_1) = -2 \Im \langle \nabla_z \chi_{v,c}, L_{v,c}^{-1} (I - P_{v,c}) (\nabla_x v_1 \chi_{v,c}) \rangle, \]

\[ R_{v_1} = 2 \int \Re (\chi_{v,c}^* L_{v,c}^{-1} (v_1 \chi_{v,c})), \]

\[ g_{v,c}^{v,c} = -2 \int_{\Gamma^*} \Im (\chi_{v,c}^* L_{v,c}^{-1} (I - P_{v,c}) \nabla_z \chi_{v,c}) \cdot q_{1,k}^{v,c} \, dk. \]
Conclusions:

- We derive the Thomas-Fermi-Maxwell model and study the half space problem.
- Effective dielectric response equation is derived in the high frequency regime of the Kohn-Sham model.
- Effective transport equations are derived in the low frequency regime of the Kohn-Sham model.

Future work:

- More realistic models in surface plasmon and semiconductor. For example, the grating surface and p-n junction.
- Electron dynamics in the presence of magnetic field.
Thank You!

Questions?