Kohn-Sham eqn (Density Functional Theory)

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Quantum Many-Body Problem

Quantum many-body systems are described by the Schrödinger equation which, for n particles in an external potential U, is

$$i\partial_t\Psi = \Big(\sum_1^n(-\Delta_{x_i} + U(x_i)) + \sum_{i<j} v(x_i - x_j)\Big)\Psi, \qquad \text{(SE)}$$

where $\Psi = \Psi(x_1, \ldots, x_n, t)$, a wave function, or probability amplitude. For $x_j \in \mathbb{R}^3$, this is a linear PDE in $3n$ dimensions.

Computations with large n hit the 'exponential wall' problem, where the computation time is exponentially increasing with n.

Density Functional Theory (DFT) provides an effective (one-particle, nonlinear) approximation to the many-body SE.

At the foundation of DFT is the Kohn-Sham equation

Ground state: Hochenberg-Kohn, Levy, Lieb (justif.), Kohn-Sham;

t-dep. DFT: Runge-Gross (justification of t-dep. Kohn-Sham eq)

Dynamical Kohn-Sham equation

Dynamics of DFT is determined by the (t-dep) Kohn-Sham eqn

$$\partial_t \gamma = -i[h_\gamma, \gamma], \tag{KSE}$$

where $\gamma = \gamma(t)$ is a family of pos., trace-class oprs (density oprs),

$h_\gamma := -\Delta + U + g(\rho_\gamma)$, with $g : L^1_{\mathrm{loc}}(\mathbb{R}^d) \to \mathbb{R}$,

U is an external potential,

$\rho_\gamma(x,t) := \gamma(x,x,t)$, the one-particle density,
$g(\rho) = v * \rho + xc(\rho)$ is self-interaction energy, with
- v a pair potential, say the Coulomb potential, $c/|x|$,
- xc(ρ) the exchange-correlation energy.

Trade-off: large dimensions for the nonlinearity.

Theory: Existence of $xc(\rho)$, but not its form (Runge-Gross)

Math Phys: Bounds on $xc(\rho)$ (Lieb, Lewin, Seiringer)

Quant Chem./Phys. : Design $xc(\rho)$ depending on a model

Our approach: Class of $xc(\rho)$'s which hopefully contains the true and its interesting approximations

Properties of the Kohn-Sham equation (KSE)

- Conservation of energy and number of particles

$$E(\gamma) := \mathrm{Tr}(h\gamma) + G(\rho_\gamma), \tag{1}$$

$$N(\gamma) := \mathrm{Tr}\,\gamma = \int \rho_\gamma, \tag{2}$$

  where $h := -\Delta + U$ and, recall, $\rho_\gamma(x,t) := \gamma(x,x,t)$ and $G(\rho)$ is an anti-L^2-gradient of $g(\rho)$, i.e. $d_\rho G(\rho)\xi = \int g(\rho)\xi dx$.

- Preservation of positivity $\gamma \geq 0$, and Pauli principle: $\gamma \leq \mathbf{1}$ (fermions),

- Hamiltonian structure with Hamiltonian $E(\gamma)$ and Poisson bracket generated by the operator $J = J(\gamma) : \xi \to i[\xi, \gamma]$ so that

$$\text{KSE} \qquad \Longleftrightarrow \qquad \frac{\partial \gamma}{\partial t} = J(\gamma)\nabla E(\gamma), \tag{3}$$

  where $\nabla E(\gamma)$ is defined by $dE(\gamma)\xi = \mathrm{Tr}(\xi \nabla E(\gamma))$ with $dE(\gamma)$ being the Gâteaux derivative of E.

Static equations

Ignoring symmetries and accidental degeneracies, γ is a static solution to KSE

$$\partial_t \gamma = -i[h_\gamma, \gamma], \tag{4}$$

if and only if γ solves $\gamma = f(h_\gamma)$ for some reasonable function f.

For a system in thermal equilibrium, $f(\lambda)$ is the Fermi-Dirac distrib:

$$f_{T,\mu}(\lambda) = \frac{1}{e^{(\lambda-\mu)/T} + 1},$$

where $T > 0$ is the temperature, μ is the chemical pot., yielding

$$\gamma = f_{T,\mu}(h_\gamma), \qquad \text{(self-consistent Gibbs/FD state)} \tag{5}$$

Theorem. Stationary solutions are critical points of the free energy

$$F_T(\gamma) := E(\gamma) - TS(\gamma), \tag{6}$$

for $N(\gamma)$ fixed, where $S(\gamma) := \operatorname{Tr} s(\gamma)$ and s any reasonable funct.

Quantum models of heat/Thermodynamic limit $\Longrightarrow$
$$s(\gamma) = -\gamma \ln \gamma - (\mathbf{1} - \gamma) \ln(\mathbf{1} - \gamma) \Longrightarrow \gamma = f_{T,\mu}(h_\gamma).$$

Density functional theory at $T > 0$

As was argued above, static DFT at $T > 0$ is given by the equation

$$\gamma = f_{T,\mu}(h_{\rho_\gamma}), \tag{7}$$

where $f_{T,\mu}(h) := (1 + e^{(h-\mu)/T})^{-1}$, the Fermi-Dirac distribution &

$$h_\rho \equiv h_\gamma := -\Delta + U + g(\rho),$$

and, recall, $\rho_\gamma(x, t) := \gamma(x, x, t)$ and $g(\rho) = v * \rho + \mathrm{xc}(\rho)$.

Rewrite (7) in terms of ρ. for this, we define the map den : operators $A \to$ functions

$$\mathrm{den}[A](x) := A(x, x).$$

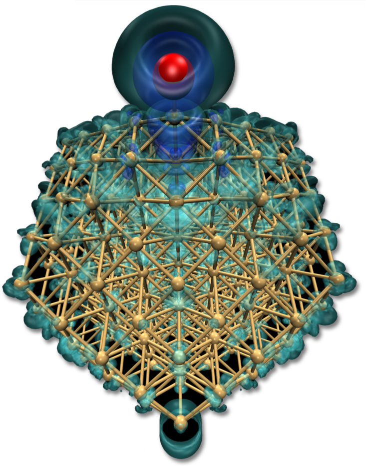
Applying den to (7), we arrive at the $T > 0$ DFT eq. in terms of ρ:

$$\rho = \mathrm{den}[f_{T,\mu}(h_\rho)]. \tag{8}$$

(8) is an extension to $T > 0$ of the key Kohn-Sham eq of DFT.

Example of some computations with the DFT

The DFT has tremendous success in describing the electronic structure of matter. An example of DFT calculation:



The isosurface of the ground-state electron density of the cuboctahedral gold clusters with adsorbed oxygen and carbon monoxide.
From: https://www.flickr.com/photos/argonne/5351929963

Macroscopic equations

Key Problem: Derive macro theories from reliable micro models

With tremendous success in describing the electronic structure of matter, it is natural to use the DFT as a starting point.

Below, I describe a derivation of the *electrostatic* eq and *permittivity matrix* in dielectrics from the DFT eq at $T > 0$.

Physical model: macroscopic perturbation of (microscopic) crystals. A crystal is described by the ionic charge distribution κ. The corresponding potential energy is $U = -v * \kappa$, where v is the Coulomb potential.
KSE for electrons and ions with the charge distributions ρ and κ:

$$\rho = \mathrm{den}[f_{T,\mu}(h_\rho^\kappa)]. \tag{9}$$

where

$$h_\rho^\kappa := -\Delta - v * (\kappa - \rho) + \mathrm{xc}(\rho).$$

Perfect crystals in DFT

We describe a perfect crystal is by a positive ionic charge distribution κ periodic w.r. to a lattice $\mathcal{L}$ in $\mathbb{R}^3$.

Define the Sobolev spaces

$$H^s_{\mathrm{per}}(\mathbb{R}^3) := \{f \in H^s_{\mathrm{loc}}(\mathbb{R}^3) : f \text{ is } \mathcal{L}\text{-periodic}\}\,. \tag{10}$$

Theorem (∃ DFT crystal). Let $T > 0$, $\kappa = \kappa_{\mathrm{per}} \in H^2_{\mathrm{per}}(\mathbb{R}^3)$ and technical conditions on the *xc* hold. Then the KS equation

$$\rho = \mathrm{den}[f_{T,\mu}(h^\kappa_\rho)]$$

has $\mathcal{L}-$per, free-energy minim. soln $(\rho_{\mathrm{per}}, \mu_{\mathrm{per}}) \in (H^2_{\mathrm{per}}(\mathbb{R}^3), \mathbb{R})$.

Self-consistent (DFT) dielectrics

An $\mathcal{L}$-periodic background charge density $\kappa_{\rm per} \in L^2_{\rm per}(\mathbb{R}^3)$ is a '(DFT) dielectric' density iff the $\mathcal{L}$-periodic solution $(\rho_{\rm per}, \mu_{\rm per})$ of the Kohn-Sham eq. with $\kappa = \kappa_{\rm per}$ satisfies

(a) Schrödinger operator $h^{\kappa_{\rm per}}$ has a gap in its spectrum,

(b) $\mu_{\rm per}$ is in this gap.

Here $h^{\kappa_{\rm per}}$ is the self-adjoint periodic 1-particle Schrödinger opr

$$h^{\kappa_{\rm per}} := -\Delta - \phi_{\rm per} \text{ on } L^2(\mathbb{R}^3), \tag{11}$$

with the periodic electric potential

$$\phi_{\rm per} := (-\Delta)^{-1}(\kappa_{\rm per} - \rho_{\rm per}). \tag{12}$$

Theorem (∃ DFT dielectrics). The map $\kappa_{\rm per} \to (\rho_{\rm per}, \mu_{\rm per})$ satisfying (a)-(b) is surjective.

Macroscopic deformations

Consider the KS (DFT) eq with a background charge distribution

$$\kappa_\delta(y) = \kappa_{\rm per}(y) + \delta^3\kappa'(\delta y), \tag{13}$$

where $\delta =$(micro scale)/(macro scale), $\kappa_{\rm per} \in H^2_{\rm per}(\mathbb{R}^3)$ and $\kappa'(x)$ is a 'macroscopic' perturbation (deformation of the crystal).

Assume $T > 0$ and technical conditions on the *xc* and the conds

- (dielectric) $\kappa_{\rm per} \in H^2_{\rm per}(\mathbb{R}^3)$ is dielectric
- (perturbation) $\kappa' \in (H^2 \cap \dot{H}^{-2})(\mathbb{R}^3)$
- (scaling) $c_T := T^{-1}e^{-\eta/T} \ll 1$, $c_T^{-8/9}\delta \ll 1$
  $(\eta = |\text{gap}(h^{\kappa_{\rm per}})|)$

Dielectric response

Theorem (Macro electrostatic eq.). Under the conditions above:
(i) the KS equation has a unique solution, $\rho_\delta(y)$, near $\rho_{\rm per}(y)$,

(ii) the electrostatic potential ϕ_δ of ρ_δ is of the form

$$\phi_\delta(y) = \underbrace{\phi_{\rm per}(y)}_{\text{micro struct}} + \underbrace{\delta\phi(\delta y)}_{\text{macro overlay}} + O_{L^2}(\delta^{7/8}),$$

where $\phi_{\rm per} \in H^2_{\rm per}(\mathbb{R}^3)$ and $\phi(x) \in H^2(\mathbb{R}^3)$ and satisfies

$$(-\operatorname{div}\epsilon\nabla + \nu^2)\phi = \kappa', \tag{14}$$

with $\epsilon = \epsilon(T) \geq 1$, a constant, real, symmetric 3×3 matrix - *permittivity matrix*, and $\nu > 0$ (the *Debye-Hückel parameter*).

The screening ν in (14) is due to the electrons at the tail of the *Fermi-Dirac distribution* falling into the *conduction* band.

Dielectric Constant (permittivity)

Dielectric constant at room temperature

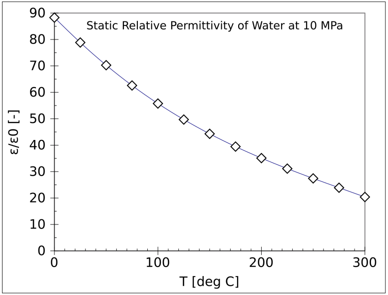
vacuum: 1

rubber: 7

silicon: 11.68

calcium copper titanate > 250.000

Temperature dependence for water at 10 MPa



Main steps of the proof: Dual representation

Pass to the dual problem KSE(ρ) $\Longrightarrow$ KSE(ϕ), where $\phi = v * (\kappa - \rho)$, the electrostatic potential generated by ρ:

$$-\Delta\phi = \kappa - \mathrm{den}[f_{T,\mu}(h^{\phi})]. \tag{15}$$

Here κ is a background charge distribution, $f_{T,\mu}(\lambda)$ is the Fermi-Dirac distribution, and

$$h^{\phi} = -\Delta - \phi + \mathrm{xc}(\kappa + \Delta\phi)). \tag{16}$$

The charge density ρ is reconstructed from ϕ via the equation

$$\rho = \kappa - \Delta\phi. \tag{17}$$

Remarks. (a) (15) follows from Poisson eq $-\Delta\phi = \kappa - \rho$ and KSE(ρ) which can be rewritten as $\rho = \mathrm{den}[f_{T,\mu}(h^{\phi})]$.

(b) (15) is a fixed point problem for ϕ. However, the linearized opr is not invertible and the standard contraction argument does not work.

Main steps of the proof: macro-micro decomposition

Smooth-rough (long-short scales, micro-macro) decomposition. Let $\phi_{\rm per}$ be periodic electric pot.l due to the background charge $\kappa_{\rm per}$. Define φ by

$$\phi = \phi_{\rm per} + \varphi. \tag{18}$$

Let $\delta =$(micro scale)/(macro scale). Define the orthogonal projections onto low and high momenta (cf [E. Cancès, M. Lewin, G. Stoltz])

$$P_r^\delta = \chi_{\{|i\delta\nabla| \le r\}} \text{ and } \bar{P}_r^{\ \delta} = \mathbf{1} - P_r^\delta = \chi_{\{|i\delta\nabla| \ge r\}} \tag{19}$$

and split φ in (18) as $\varphi = \varphi_s + \varphi_l$, with $\varphi_s := P_r\varphi$ and $\varphi_l := \bar{P}_r\varphi, \Longrightarrow$

$$\phi = \phi_{\rm per} + \varphi_s + \varphi_i. \tag{20}$$

Use the Lyapunov-Schmidt deco., with proj. P_r^δ to split (15) into two eqs

$$P_r^\delta\big[-\Delta\phi + \mathrm{den}[f_{T,\mu}(h^\phi)]\big] = P_r^\delta\kappa, \tag{21}$$

$$\bar{P}_r^{\ \delta}\big[-\Delta\phi + \mathrm{den}[f_{T,\mu}(h^\phi)]\big] = \bar{P}_r^{\ \delta}\kappa. \tag{22}$$

Since $-\Delta\bar{P}_r^{\ \delta} \ge (r/\delta)\bar{P}_r^{\ \delta}$ is huge, we can use IFT to solve (22) for φ_l. Substitute the result in (21) to obtain an eqn for φ_s leading to the PB eq.

Poisson-Boltzmann equation

The screened Poisson equation we derived is the *Debye-Hückel eq*, the linearization of the celebrated Poisson-Boltzmann eq (PBE):

$$-\nabla\epsilon\nabla\psi = \rho^{\mathrm{ext}} - \sum_i c_i z_i e^{-z_i\psi/T}, \tag{23}$$

describing the molecular potential in an ionic solvent.

Here ϵ is the dielectric constant of the solvent medium,
$\rho^{\mathrm{ext}}(x)$ is external molecular charge density,
c_i and z_i are the concentrations and charges of type i ions at infinity and T the temperature ($k = 1$).

PBE is the main tool in physical chemistry and molecular biology in describing the biomolecular systems and processes, e.g. proteins and their stability and folding pathways.

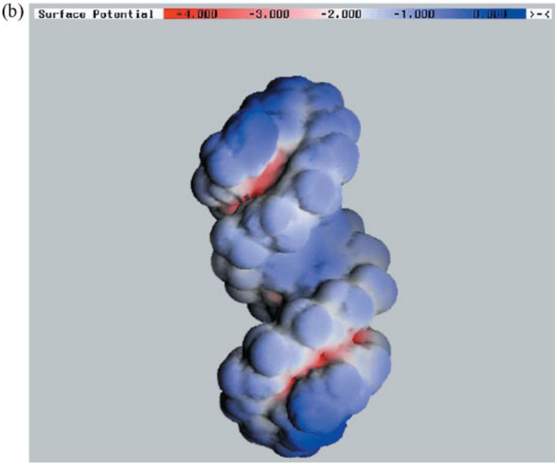


Plate 1. Electrostatic surface potential for a short B-DNA (pdb id. 9ANT, chains C and D) assuming a homogeneous ion-free medium (with dielectric constant of 80; panel a) and in 150 mM ionic strength with a solute dielectric constant of 4 (panel b). The ranges of the potential (-9.0 to -5 kcal mol^{-1} q^{-1} and -4.0 to 0.0 kcal mol^{-1} q^{-1} in the left and right panels, respectively) have been chosen for comparison.

Open problem: Derive full Poisson-Boltzmann eq. from the DFT.

Summary

We discussed

- the time-dependent and static Kohn-Sham (DFT) equations
- existence of the Gibbs (equilibrium) states at $T > 0$ for perfect and deformed crystals
- emergence of the macroscopic, effective equation for the electric potential - the Debye-Hückel eq
- the Poisson-Boltzmann equation from which the Debye-Hückel equation originates by the linearization
- derivation of *permittivity matrix*

	Web of Science	MathSciNet	Ratio
Boltzmann equation	29 915	5 472	18%
Maxwell equations	29 478	4 489	15%
Navier Stokes	63 198	24 883	39%
Density Functional Theory	211 149	468	0.2%

Thank-you for your attention