

MATHEMATICAL THEORY OF SOLIDS: FROM QUANTUM MECHANICS TO CONTINUUM MODELS

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The objective of this program is to understand the microscopic (atomistic, electronic) foundations of macroscopic (continuum) models of solids. This is a status report on the progresses that have been made and the challenges that remain. There are several motivations for such an initiative. One is intellectual: Similar program for fluids (from kinetic theory or molecular dynamics to Euler or Navier-Stokes equations) has been a major driving force in mathematics, particularly in applied analysis. The second motivation is a more practical one: Solids exhibit a variety of physical properties (mechanical, thermal, electro-magnetic) and there exist a huge number of models, mostly ad hoc, for describing these properties. Some of these properties clearly have their origin at the microscopic level. For example, whether a solid is a metal or insulator is determined by the underlying electronic structure, and this in turn also affects the mechanical and thermal properties of the material. At the atomistic level, solid are crystal lattices. The lattice structure as well as the defects of the lattices directly influence the macroscopic properties.

The idea of trying to connect macro and microscopic models of solids goes back to Cauchy [8, 9] in the 1820's. Assuming that the atoms in solids interact via a two-body central potential, i.e. the potential depends only on the distance between pairs of atoms, Cauchy derived expressions for the elastic moduli of cubic crystals. In particular, he discovered the well-known Cauchy relation:

$$C_{12} = C_{44}.$$

However, this relation is violated by most, if not all, elemental solids (see for example [20, Page 291]). This tells us that Cauchy's model of inter-atomic potential is a bad approximation.

Born extended Cauchy's work to more sophisticated models and crystal lattices. He formulated the so-called Cauchy-Born rule, which is a central object that we will discuss below. In addition, Born initiated a systematic study of the microscopic origin of macroscopic properties of solids. The book of Born and Huang: "Dynamical Theories of Crystal Lattice" (1954) has been the classic reference of the subject.

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Mathematics literature on this problem has been thin. Blanc, Le Bris and Lions [3] considered continuum limit of some atomistic models and the Thomas-Fermi-von Weizsacker model, and proved *consistency* of the Cauchy-Born rule. Friesecke and Theil [16] considered a lattice-spring model and proved that minimizers may *not* satisfy the Cauchy-Born rule. Other related work has been done by Braides, Cances, Conti, Dal Maso, Lewin, Müller, etc. [5, 6, 10]

1. Continuum models of solids. There are a variety of continuum models for solids, covering different aspects of material properties. The following list is far from being complete.

- mechanical properties (elasticity, plasticity,...)
 - Linear elasticity: $\rho \frac{\partial^2 u}{\partial t^2} = (\lambda + \mu) \nabla(\nabla \cdot u) + \mu \Delta u$
 - Nonlinear elasticity: $\inf \int_{\Omega} (W(\nabla u(x)) - f(x)u(x)) dx$
 - Plasticity:
- heat conduction (Fourier's law)
- electro-magnetic response (polarization, magnetization, transport of electro-magnetic fields)
 - Maxwell's equation, Landau-Lifshitz, ...

Of course, all these different properties may very well be coupled. For example, stress may influence the electro-magnetic response. There are a variety of models that have been proposed to describe such coupling.

2. Microscopic models.

2.1. Quantum mechanics models. We will neglect spin in this presentation. Although there exist some results that deal with spins (see for example [12]), this is still a relatively unexplored area. In particular, the Dirac-Kohn-Sham equation, the analog of Kohn-Sham equation that includes spins, is still a mathematically challenging problem due to its negative energy states.

For most, if not all, of our purposes it is enough to treat the nuclei classically and the electrons quantum mechanically. In such a setting, there are three different levels of quantum mechanics models.

1. Quantum many-body problem. The main object is the many-body wavefunction $\Psi : \mathbb{R}^{3N} \rightarrow \mathbb{C}$. The physical model is the Schrodinger equation. This is the true first principle. But at the moment, it is too complicated to use for either analytical or practical purposes.
2. The other extreme is the Thomas-Fermi type of models, or more generally, orbital-free models. The main object for this class of models is the electron density $\rho : \mathbb{R}^3 \rightarrow \mathbb{R}$. The energy for the Thomas-Fermi-von Weizsacker-Dirac model reads:

$$I(\rho) = \varepsilon^2 \int_{\mathbb{R}^3} \rho^{5/3} dy + \varepsilon^2 \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 dy + \frac{\varepsilon}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{(\rho - m)(y)(\rho - m)(y')}{|y - y'|} dy dy' - \varepsilon \int_{\mathbb{R}^3} \rho^{4/3} dy$$

The parameter ε and the background charge m will be explained below. This type of models takes the form of a conventional variational problem, even though it is still highly non-linear and non-convex. However, it is too inaccurate and it lacks some important quantum characters such as band structure.

3. Kohn-Sham density functional theory or Hartree-Fock theory. The main object for these models are the coupled one-body wavefunctions $\{\psi_1, \dots, \psi_N\}$. They are the true work-horse for first principle-based study of materials and molecules. The Kohn-Sham density functional theory has been particularly popular for materials modeling.

Let us now explain the Kohn-Sham density functional theory (DFT) [17, 18] in more details. The energy functional for a system with N electrons takes the form:

$$I(\{\psi_k\}) = \varepsilon^2 \sum_{k=1}^N \int_{\mathbb{R}^3} |\nabla \psi_k(y)|^2 dy + \int_{\mathbb{R}^3} \epsilon_{xc}(\rho) \rho(y) dy + \frac{\varepsilon}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{(\rho - m)(y)(\rho - m)(y')}{|y - y'|} dy dy'. \tag{1}$$

where $\{\psi_k = \psi_k(y), k = 1, \dots, N\}$ are a set of N orthonormal wavefunctions. Here

$$\rho(y) = \sum_k |\psi_k(y)|^2$$

is the electron density, m is the background charge density from the nuclei. It takes the form:

$$m(y) = \sum_{y_j \in \Omega} m_j^a(y - y_j),$$

where $\{y_j\}$ is the position of the j -th nucleus, $\{m_j^a\}$ is the ionic potential describing the j -th nucleus, assumed to be smooth and decay to 0 sufficiently fast. Using physicists' terminology, we have taken a local pseudopotential approximation.

The parameter ε is some atomic length scale, e.g. the lattice constant. Introducing this parameter means that we have used the macroscopic units, i.e. the size of the physical domain occupied by the material is taken to be $\mathcal{O}(1)$ and the lattice parameter of the solid is taken to be $\mathcal{O}(\varepsilon) \ll 1$. In contrast, in microscopic units, the size of the unit cell of the solid is $\mathcal{O}(1)$ and the size of the whole material is $\mathcal{O}(1/\varepsilon)$. In any case, the number of electrons N scales as $1/\varepsilon^3$ as ε goes to 0.

ϵ_{xc} in (1) is the *exchange-correlation energy density functional*. The Hohenberg-Kohn theorem states that there exists a universal exchange-correlation functional. However, it does not tell us what it actually is. So much of the work in DFT goes into constructing this functional. The very success of DFT hinges on the fact that relatively simple functionals can give rise to acceptable accuracy. Here we will limit our attention to the case of *local density approximation*, i.e. ϵ_{xc} is a functional of the local density only $\epsilon_{xc} = \epsilon_{xc}(\rho)$.

The Euler-Lagrange equation associated with (1) reads

$$\left(-\frac{\varepsilon^2}{2} \Delta + V[\rho]\right) \psi_i = \lambda_i \psi_i, \tag{2}$$

where given the density ρ , the effective potential $V[\rho]$ is defined by:

$$V[\rho] = \varepsilon \int \frac{(\rho - m)(y)}{|x - y|} dy + \epsilon_{xc}(\rho) + \rho \epsilon'_{xc}(\rho). \tag{3}$$

This gives us a map from density to potential.

Given the potential, the density is obtained from solving the eigenvalue problem (2) and occupying the lowest eigenstates by the Pauli exclusion principle. This gives us a map from potential to density. The composition of these two maps is the **Kohn-Sham map**, denoted as \mathcal{F}^ε , where we indicate explicitly the dependence

on the small parameter ε . Hence in Kohn-Sham DFT, the electron density of the system is then given by the fixed points of the Kohn-Sham map

$$\rho = \mathcal{F}^\varepsilon(\rho). \quad (4)$$

2.2. Classical (empirical) atomistic models. These models only have the nuclei explicitly in the picture. The nuclei interact via some inter-atomic potential. These potentials are found empirically (by fitting with experimental results or ab initio calculations).

Denote by $\{y_j\}_{j=1,\dots,M}$ the positions of the atoms. The Lennard-Jones potential is the simplest example of inter-atomic potentials, where

$$V(y_1, y_2, \dots, y_N) = \sum_{ij} V_{\text{LJ}}(|y_i - y_j|) \quad (5)$$

with

$$V_{\text{LJ}}(r) = 4E_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

where E_0 and σ are parameters. The Lennard-Jones potential only has pairwise interactions between atoms. Other popular examples include Stillinger-Weber, EAM (embedded atom model) potential include many-body interactions between atoms.

The key question that we are interested in include:

- Are these models on different physical levels consistent with each other? Can we derive simpler models from more complex ones?
- What is each model good for?

3. From atomistic models to elasticity theory. The first problem we will discuss is the derivation of nonlinear elasticity models from atomistic models for static problems.

Recall that continuum models of nonlinear elasticity usually take the form:

$$I(v) = \int_{\Omega} \{W(\nabla v) - f(x)v(x)\} dx$$

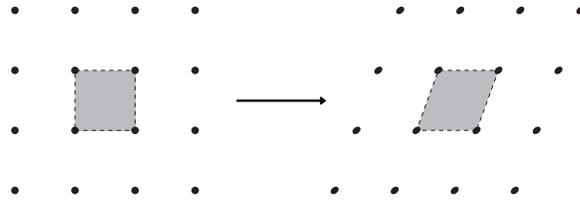
where v is the displacement field, i.e. after deformation a material point at x is moved to $y = x + v(x)$. W is the *stored energy density*. The key question is: what is W ? Usually W is manufactured empirically with constraints coming from symmetry or invariance. Our aim in this section is to derive W from atomistic models.

The atomistic models that we will consider take the form:

$$I_N(\{y_j\}) = V(y_1, \dots, y_N) - \sum f(x_j)v_j$$

where x_j, y_j are the positions of the j -th atom before/after deformation, $v_j = y_j - x_j$ is the displacement of the j -th atom. The first term on the right is the potential energy due to inter-atomic interaction. The second term is the work done by the applied forcing. f is the field of applied forcing. This form is slightly less natural than, say, $\sum f(y_j)v_j$. But this latter form will lead to a nonlinear term for the forcing, which is an unessential complication that we will avoid.

3.1. The Cauchy-Born rule. The Cauchy-Born rule is a recipe for specifying the function W using the atomistic model at zero temperature. Denote by $\{x_j\}$ the equilibrium configuration of the crystal. For a simple lattice, the Cauchy-Born rule works as follows. Given A , a 3×3 matrix, we consider a uniformly deformed crystal: $y_j = x_j + Ax_j = (I + A)x_j$. $W_{CB}(A)$ is then defined to be the energy density of deformed unit cell, computed according to the given atomistic model.



For complex lattices, each unit cell contains more than one atom, giving rise to additional degrees of freedom. It is common to model these addition degrees of freedom by the shift vectors p_1, \dots, p_k , which specify the relative positions of the atoms in the unit cell with respect to a reference atom in the cell. We can then define $W(A, p_1, \dots, p_k)$ to be the energy density of a lattice obtained by deforming the basis vectors with uniform deformation gradient A and placing the shift vectors at the positions p_1, \dots, p_k respectively. The Cauchy-Born energy density is then given by $W_{CB}(A) = \min_p W(A, p_1, \dots, p_k)$, i.e. the energy density is minimized with respect to the internal degree of freedom within the unit cell, represented by the shift vectors, after the lattice is homogeneously deformed.

The Cauchy-Born rule is a key component in some versions of the quasi-continuum method [22]. Its various extended forms have also been used to derive continuum models of nano-structures such as nano-tubes [1, 2, 23].

3.2. The stability conditions for elastically deformed states. We next discuss the work of E and Ming on the validity of the Cauchy-Born rule [15]. The key issue is the stability condition. This has been a source of some controversies in the physics literature. Two types of stability conditions have been proposed. The Born stability condition is about the positive definiteness of the elastic stiffness tensor [4]. Lindemann studied this problem from the viewpoint of the melting of the crystal lattice. He proposed a stability condition based on the vibrational amplitude of the crystal lattice [19]. We will see that both conditions are needed.

Stability condition I: The elastic stiffness tensor defined by the Cauchy-Born stored energy density is positive definite:

$$C = \nabla_A^2 W_{CB}(0) > 0.$$

Under this condition it is well-known that the variational problem:

$$I(v) = \int_{\Omega} \{W_{CB}(\nabla v) - f(x)v(x)\} dx$$

is well-posed. A version of the well-posedness is given by the following Lemma.

Lemma. ($p \geq d = \text{dimension}$). Assume that the first stability condition holds. Then $\exists K, R$ such that if $\|f\|_{L^p} \leq K$, then \exists a unique local $W^{1,\infty}$ -minimizer, $v = u_{CB}$, such that

$$\|u_{CB}\|_{W^{2,p}} \leq R$$

The second condition is about the phonon spectra of the crystal lattice. The phonon spectra are given by the dispersion relation of the Hessian of the atomistic energy at the equilibrium crystalline state. For simple lattice, the phonon spectra only has the acoustic branch describing the vibration of the whole lattice. For complex lattice, the phonon spectra also has the optical branches which describe the relative motion between atoms inside the unit cell.

Stability condition II: $\exists \Lambda_1, \Lambda_2 > 0$. For $k \in$ first Brillouin zone,

$$\omega_a(k) \geq \Lambda_1 |k|, \quad \omega_o(k) \geq \Lambda_2,$$

where $\omega_a(k)$ and $\omega_o(k)$ give the dispersion relation of the acoustic phonon branch and optical phonon branch respectively.

Theorem 1 (E-Ming [15]). *Assume that*

1. *the inter-atomic potential is finite ranged,*
2. *both stability conditions hold.*

and the boundary conditions is given by periodic boundary condition with a possible global linear tilt. Then there exists a unique local minimizer y_ϵ of the atomistic model, such that

$$\|y_\epsilon - y_{CB}\|_1 \leq C_0 \epsilon,$$

where $\|\cdot\|_1 =$ discrete H^1 norm, and $y_{CB}(x) = x + u_{CB}(x)$ with u_{CB} the solution to the Cauchy-Born elasticity problem.

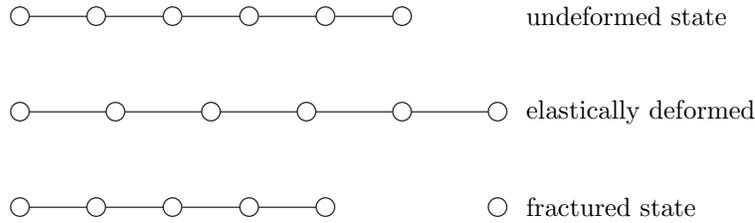
Note: The work [15] contains a sharp version of this result: “As long as the stability conditions hold, then the Cauchy-Born rule gives accurate approximation for the deformation of the crystalline solid”.

It is of interest to compare this result with the one proved in the work of Blanc, Le Bris and Lions [3]. Assuming that the deformation is smooth, i.e. $y_j = x_j + u(x_j)$, where u is smooth, [3] studied the continuum limit of a large class of atomistic energy functionals and recovered the Cauchy-Born rule. The spirit of their results is that the atomistic energy functional can be viewed as a Riemann sum for the Cauchy-Born continuum functional. In the language of numerical analysis, their result is about the consistency of the atomistic model with the Cauchy-Born continuum model. Convergence requires stability.

As a concrete model, consider Lennard-Jones potential with next nearest neighbor interaction. It can be shown by a direct calculation that on a triangular lattice, the stability conditions hold and consequently the Cauchy-Born is valid. But on a square lattice, the elastic shear modulus is negative. Therefore the first stability condition is violated. In this case, one can not speak of an elastic continuum limit, not to mention the Cauchy-Born rule. Atomistic simulations have clearly shown this. Of course, consistency holds in both cases.

Another important remark is that we have to deal with local minimizers. This is explained by the following example. Consider the stretching of a chain of atoms by moving the rightmost atom by a distance D_0 to the right, holding the leftmost atom fixed. An easy calculation leads to the conclusion that the energy of the elastically deformed state is $E_1 \sim NV_0(1 + D_0/L)$, while the energy of the fractured state $E_2 \sim V_0(1 + D_0/\epsilon)$, and hence has less energy when N is large! Therefore to obtain elastically deformed state, one has to consider local minimizers.

An interesting question arises as to why solids do not spontaneously fracture under extensive stress. The answer has to be that elastically stressed states are



local minimizers and the energy barrier for moving to the fractured states is too high. Therefore over the time scale we are interested in, solids do not fracture.

Another interesting question is: *What happens when ideal crystals become unstable?* In this direction, some interesting work has been done by Xiaotao Li (unpublished). See also the related works of Ryan Elliot, Ju Li, Steven Louie, etc.

4. Continuum limit of the Kohn-Sham density functional theory. Next we get the electrons into the picture. A natural starting point is the Kohn-Sham density functional theory. This study will be carried out in two steps:

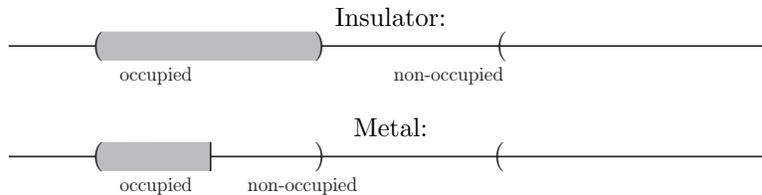
Step 1. Study the structure of the electrons giving the position of the ions (atoms, i.e. of a deformed crystal) in the spirit of Born-Oppenheimer approximation. This is the work of E and Lu that we will report below.

Step 2. Let both the ions and electrons move. This is ongoing work of Lu.

4.1. Electronic structure stability. Let us start with the band structure for the periodic crystal system. This is obtained by solving the Schrödinger equation (for non-interacting electrons in a crystal):

$$-\Delta\psi(x) + V_{\text{eff}}(x)\psi(x) = \lambda\psi(x), \quad x \in \mathbb{R}^3 \tag{6}$$

Note that V_{eff} is periodic (due to the crystal structure), this problem has only continuous spectrum, which forms the band structure (as a result of the Bloch-Floquet theory) [21] $\text{spec } H = \bigcup_n \bigcup_{\xi \in \Gamma^*} E_n(\xi)$ with the corresponding Bloch waves $u_{n,\xi}(x)$ that are periodic on the unit cell. The Fermi level is determined by filling the band structure by electrons according to Pauli’s exclusion principle. According to whether the spectrum has a gap at the Fermi level, the system is either an insulator or a metal.



Stability condition IIIa: Existence of a band-gap in the band structure for the undeformed lattice. In physics language, the material is an insulator.

The requirement of this stability condition can be understood as otherwise the (non-compact) perturbation caused by the elastic deformation might open spectrum gap for metallic systems.

For insulating systems under elastic deformation, the Kohn-Sham map can be formulated as:

$$\rho(x) = \mathcal{F}_u^\varepsilon(\rho)(x) = \frac{1}{2\pi i} \int_C \frac{1}{\lambda - H_u^\varepsilon[\rho]} d\lambda(x, x),$$

where $\frac{1}{\lambda - H_u^\varepsilon[\rho]}$ is the resolvent of the operator and hence the right hand side denotes the diagonal of the kernel of the spectral projection operator, \mathcal{C} is a fixed contour in the resolvent set of the Hamiltonian (of the undeformed system) enclosing the occupied spectrum. When the deformation is not large, the occupied spectrum stays within the contour \mathcal{C} . The effective Hamiltonian is given by

$$H_u^\varepsilon[\rho] = -\frac{\varepsilon^2}{2}\Delta + \varepsilon \int \frac{(\rho - m)(y)}{|x - y|} dy + \rho \epsilon'_{xc}(\rho) + \epsilon_{xc}(\rho).$$

Here u denotes the elastic deformation of the atoms (recall that atoms are fixed in the study here): The problem depends on u through the background ionic charge:

$$m(y) = \sum_{y_j \in \Omega} m_j^a(y - y_j), \quad y_j = x_j + u(y_j).$$

The analog of the phonon spectra at the electronic level is the plasmon spectrum (for the undeformed lattice). The associated stability condition reads.

Stability condition IIIb: The undeformed crystal is stable with respect to charge density wave (plasmon) perturbations.

Mathematically, this condition means that if we linearize the Kohn-Sham map $\mathcal{F}_u^\varepsilon$ around the undeformed state, the resulting linear operator is invertible in a suitable Sobolev space. More precisely, the linearization of the Kohn-Sham map at the equilibrium state is given by

$$(\mathcal{L}_e w)(x) = \frac{1}{2\pi i} \left(\int_{\mathcal{C}} \frac{1}{\lambda - H_e} (\delta_{\rho_e} V_e)(w) \frac{1}{\lambda - H_e} d\lambda \right) (x, x), \tag{7}$$

where H_e is the effective Hamiltonian operator at the undeformed state and $\delta_{\rho_e} V_e$ is the linearized effective potential operator at equilibrium.

The stability condition can be understood in terms of the linear operator \mathcal{L}_e . It is established in [13] that \mathcal{L}_e is a bounded linear in the Sobolev space $\dot{H}_{\#}^{-1}(n\Gamma) \cap H_{\#}^2(n\Gamma)$ for every $n \in \mathbb{N}$, where $H_{\#}(n\Gamma)$ stands for Sobolev spaces with periodic boundary condition on the domain $n\Gamma$, n times the unit cell of the lattice. \dot{H}^{-1} is the homogeneous Sobolev space with index -1 , also known as the Coulomb space. Mathematically, the stability condition IIIb reads: For every $n \in \mathbb{N}$, $\mathcal{I} - \mathcal{L}_e$ as an operator on $\dot{H}_{\#}^{-1}(n\Gamma) \cap H_{\#}^2(n\Gamma)$ is uniformly invertible with respect to n .

Note that this is analogous to the situation in nonlinear homogenization, where we need to consider stability of cell problems at arbitrary length scale, as n varies.

We also need a stability condition which is the analog of the Born stability condition on the electromagnetic side.

Stability condition IIIc: The permittivity tensor (see below) for the undeformed crystal is positive definite (The effective Poisson equation is elliptic).

The macroscopic permittivity tensor is given by

$$\mathbb{E}_e = \frac{1}{2}(\mathbb{A}_e + \mathbb{A}_e^*) + \frac{1}{4\pi} \mathbb{1},$$

where \mathbb{A}_e is given by for $\alpha, \beta = 1, 2, 3$:

$$\begin{aligned} A_{e,\alpha\beta} = & -2\Re \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{E_n(\xi) - E_m(\xi)} \overline{\langle u_{m,\xi}, \partial_{\xi,\beta} u_{n,\xi} \rangle} \langle u_{m,\xi}, \partial_{\xi,\alpha} u_{n,\xi} \rangle \\ & - \langle g_{e,\alpha}, \delta_{\rho_e} V_e (\mathcal{I} - \mathcal{L}_e)^{-1} g_{e,\beta} \rangle, \end{aligned}$$

with

$$g_{e,\alpha}(z) = 2\Re \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{E_n(\xi) - E_m(\xi)} u_{n,\xi}^*(z) u_{m,\xi}(z) \langle u_{m,\xi}, i\partial_{\xi_\alpha} u_{n,\xi} \rangle.$$

Here Z is the number of occupied bands (the number of electrons per unit cell), $(E_n(\xi), u_{n,\xi})$ are the eigen-pair given by the Bloch eigenvalue problem on Γ with periodic boundary condition:

$$(e^{-i\xi \cdot x} H_e e^{i\xi \cdot x}) u_{n,\xi} = E_n(\xi) u_{n,\xi}$$

for ξ in the first Brillouin zone Γ^* . This formula gives the macroscopic permittivity of the undeformed crystal by the Kohn-Sham density functional theory, see also [6] for the study of dielectric tensor for reduced Hartree-Fock theory.

We now state the main result for the Cauchy-Born rule at the electronic structure level.

Theorem 2 (E-Lu [11, 13]). *Assume periodic boundary condition for the macro domain. Under the stability conditions, there exist constants a_0, A_0, ε_0 and M , such that if $\varepsilon \leq \varepsilon_0$ and if $M_A = \sup_j \|\nabla^j u\|_{L^\infty} \leq a_0$, then there exists $\rho^\varepsilon \in L^\infty$ with the property:*

- ρ^ε is a solution to the Kohn-Sham equation:

$$\rho^\varepsilon(x) = \mathcal{F}_\tau^\varepsilon(\rho^\varepsilon)(x).$$

- There is a well-defined Cauchy-Born electron density $\rho_{CB}(\cdot; A)$, if $\|A\| \leq A_0$.
- $\|\rho^\varepsilon - \varepsilon^{-3} \rho_{CB}(x/\varepsilon; \nabla u(x))\|_{L^\infty} \leq M\varepsilon^{1/2}$, i.e., $\|\tilde{\rho}^\varepsilon - \rho_{CB}(x; \nabla u(\varepsilon x))\|_{L^\infty} \leq M\varepsilon^{1/2}$, where $\tilde{\rho}^\varepsilon(x) = \varepsilon^3 \rho^\varepsilon(x)$, and ρ^ε satisfies the normalization constraint:

$$\int_{\Gamma} \rho^\varepsilon(x) \, dx = Z\varepsilon^{-3}.$$

where Z is the total nuclear charge of the unit cell.

- Moreover, The macroscopic potential satisfies a second-order elliptic equation of the form:

$$A_{\alpha\beta} \partial_{x_\alpha} \partial_{x_\beta} U_0(x) + \frac{1}{4\pi} L_2 U_0(x) + B_\alpha \partial_{x_\alpha} U_0(x) + D - \langle m_2(x, \cdot) \rangle = 0.$$

The coefficients can be computed from the deformation gradient. $A_{\alpha\beta}$ gives the permittivity tensor for a homogeneously deformed crystal. Note that this is a piezo-electric effect: mechanical deformation is coupled to perturbation of electric potential.

Here the Cauchy-Born electron density $\rho_{CB}(\cdot; A)$ is the electron density obtained from the Kohn-Sham density functional theory for a homogeneously deformed crystal (with deformation gradient A). Due to the periodicity, this can then be reduced to a problem defined only on the unit cell (as opposed to the whole space). This is analogous to solving cell problems in standard homogenization problems.

Comments on the proof. The proof is based on (1) uniform estimates for the linearized Kohn-Sham map and (2) constructing approximate solutions to the Kohn-Sham equation for deformed crystal that are accurate up to high order.

Constructing approximate solutions turns out to be highly nontrivial due to the Coulomb term, which amplifies the perturbation in the density as we are dealing with large physical domain as $\varepsilon \rightarrow 0$. One of the key observation is that we can decompose the contribution from the Coulomb interaction into short and long range parts; using the locality properties associated to the Green's function for insulating

systems, the short range part does not impact the electron density at a distance. This enables us to construct solutions that match at different orders of ε .

Starting from the approximate solution, a fixed point argument is carried out to find a solution to the Kohn-Sham equation nearby. This needs understanding of the spectral property of the linearized Kohn-Sham operator \mathcal{L}_ε , which consists of another highly nontrivial element of the proof.

5. Formal derivation of the macroscopic Maxwell's equation from time-dependent density functional theory. We have only discussed static problems so far, we now switch our focus to dynamic problems. Here we discuss a dynamic problem that involves electrons. Our aim is to derive (at least formally) macroscopic Maxwell's equation from time-dependent density functional theory [14]. See also the work of Cancès and Stoltz [7] which derives dielectric response of crystals under random phase approximation.

Consider the following model in time-dependent density functional theory:

$$\begin{aligned} i\hbar \frac{\partial \psi_j}{\partial t} &= \frac{1}{2m_e} \left(-i\hbar \nabla - \frac{e}{c} (A + A_{\text{ext}}) \right)^2 \psi_j + e(V + V_{\text{ext}}) \psi_j, \\ -\Delta \phi &= \frac{e}{\epsilon_0} (\rho - m), \\ \frac{1}{c} \frac{\partial}{\partial t} \left(\frac{1}{c} \frac{\partial}{\partial t} A + \nabla \phi \right) - \Delta A &= \frac{e}{c\epsilon_0} J, \\ \nabla \cdot A &= 0, \\ V(t, x) &= \phi(t, x) + \eta(\rho(t, x)), \end{aligned}$$

We have taken the following modeling assumptions:

- Adiabatic local density approximation for exchange-correlation scalar potential (denoted as η);
- No exchange-correlation vector potential;
- Spin degeneracy is ignored.

In the above model, the electron density and current are given by

$$\begin{aligned} \rho(t, x) &= \sum_{j=1}^N |\psi_j(t, x)|^2, \\ J(t, x) &= \frac{\hbar}{m_e} \sum_{j=1}^N \Im(\psi_j^*(t, x) \nabla \psi_j(t, x)) - \frac{e}{m_e c} \rho(t, x) A(t, x). \end{aligned}$$

The system describes the quantum dynamics of electrons under the effect of external potentials A_{ext} and V_{ext} . It consists of nonlinear Schrödinger equations (many electrons) coupled with microscopic (vacuum) Maxwell equations.

We will assume that the external fields V_{ext} and A_{ext} are slowly varying in space. After non-dimensionalization, we get

$$i \frac{\partial \psi_j}{\partial t} = \frac{1}{2} (-i\varepsilon \nabla - \varepsilon(A + A_{\text{ext}}))^2 \psi_j + (V + V_{\text{ext}}) \psi_j,$$

$$\begin{aligned}
 -\Delta\phi &= \varepsilon(\rho - m), \\
 \frac{\partial^2}{\partial t^2}A - \Delta A + \frac{\partial}{\partial t}\nabla\phi &= \varepsilon^2 J, \\
 \nabla \cdot A &= 0, \\
 V(t, x) &= \phi(t, x) + \eta(\varepsilon^3 \rho(t, x)). \\
 \rho(t, x) &= \sum |\psi_j(t, x)|^2, \\
 J(t, x) &= \varepsilon \sum \Im(\psi_j^*(t, x)\nabla\psi_j(t, x)) - \varepsilon\rho(t, x)A(t, x).
 \end{aligned}$$

Here ε is the ratio between the lattice parameter and the typical scale for the external fields.

Assume that without external fields, the ground state of the system forms a perfect lattice and is an insulator (finite gap in the spectrum), we obtain the effective Maxwell equations when $\varepsilon \ll 1$ as

$$\begin{aligned}
 \nabla \cdot (\mathcal{E}(\omega)\widehat{E}(\omega, x)) &= \widehat{\rho}_{\text{ext}}(\omega, x), \\
 \nabla \cdot \widehat{B}(\omega, x) &= 0, \\
 \nabla \times \widehat{E}(\omega, x) &= i\omega\widehat{B}(\omega, x), \\
 \nabla \times \widehat{B}(\omega, x) &= -i\omega\mathcal{E}(\omega)\widehat{E}(\omega, x) + \widehat{J}_{\text{ext}}(\omega, x),
 \end{aligned}$$

with $\rho_{\text{ext}}, J_{\text{ext}}$ given by V_{ext} and A_{ext} . Here the effective dynamic permittivity \mathcal{E} is given by the electronic structure (at equilibrium). Note that the permeability tensor is the same as that of the vacuum. More precisely, we have $\mathcal{E}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + A_{e,\alpha\beta}(\omega)$.

$$\begin{aligned}
 A_{e,\alpha\beta}(\omega) &= \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} \overline{\langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle} \langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle \\
 &\quad - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} \langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle \overline{\langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle} \\
 &\quad - \frac{2i}{\omega} \Im \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \overline{\langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle} \langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle d\xi \\
 &\quad - \left\langle g_{e,\omega,\alpha}, \delta_{\rho_e} V_e (\mathcal{I} - \chi_{e,\omega} \delta_{\rho_e} V_e)^{-1} g_{e,\omega,\beta} \right\rangle,
 \end{aligned}$$

with the short hand notation $\omega_{mn}(\xi) = \lambda_m(\xi) - \lambda_n(\xi)$ and $\delta_{\rho_e} V_e$ is the linearized effective potential operator at equilibrium. Moreover, the dynamic polarizability operator $\chi_{e,\omega}$ and the vector valued functions $g_{e,\omega}$ are given by

$$\begin{aligned}
 \chi_{e,\omega} V &= - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} u_{n,\xi} u_{m,\xi}^* \langle u_{n,\xi}, V u_{m,\xi} \rangle \\
 &\quad + \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} u_{n,\xi}^* u_{m,\xi} \langle u_{m,\xi}, V u_{n,\xi} \rangle, \\
 g_{e,\omega} &= - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} u_{n,\xi} u_{m,\xi}^* \langle u_{n,\xi}, i\nabla_\xi u_{m,\xi} \rangle \\
 &\quad + \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} u_{n,\xi}^* u_{m,\xi} \langle i\nabla_\xi u_{m,\xi}, u_{n,\xi} \rangle.
 \end{aligned}$$

6. **Open questions.** Many questions remain open. We will list a few of those.

- Stability of the electronic structure in metals
- Where does the nonlinearity in Maxwell's equation come from?
- Complete characterization of the coupling between deformation and EM response.
- Finite temperature case. In this case, we have to study the metastability of elastically deformed states.

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