Electrical conductivity of materials under extreme Conditions using TDDFT

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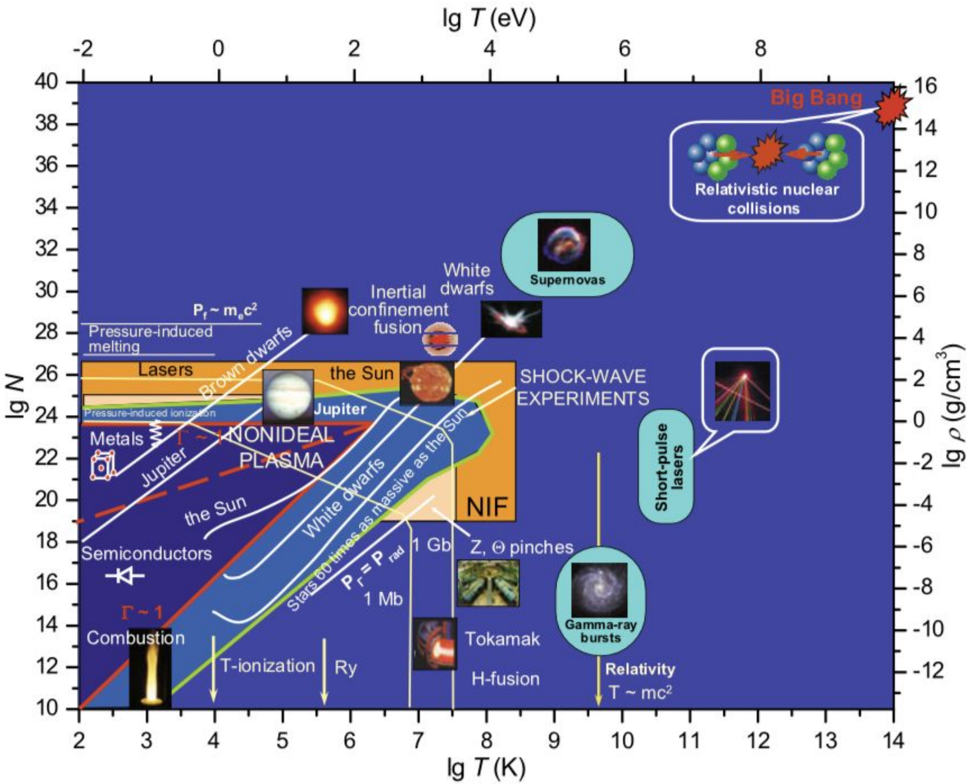
Outline

- Matter under extreme conditions
  - Earth core
  - Iron

- An assessment of several state-of-the-art modeling techniques
  - Linear response methods - LR- TDDFT, RT-TDDFT and Kubo-Greenwood formalism.

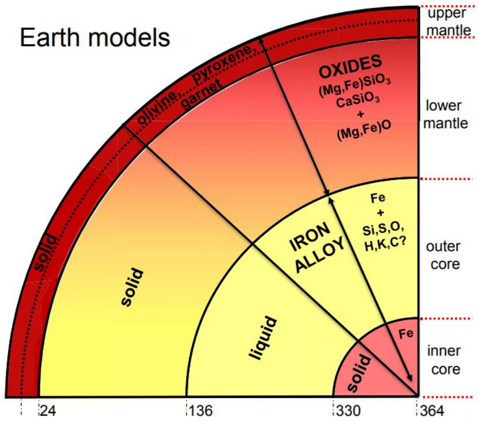
- Results
  - Ambient iron
  - Compressed iron

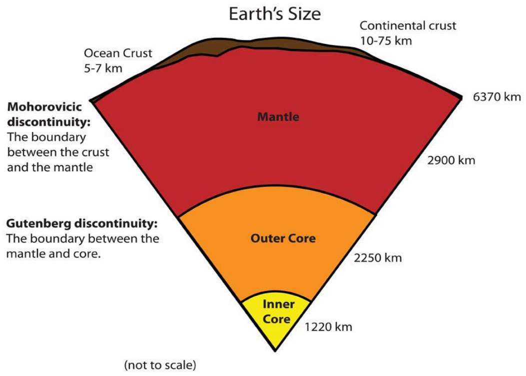
Matter under extreme conditions



Extreme States of Matter on Earth and in the cosmos - Vladimir Fortov, Springer (2011)

Earth core

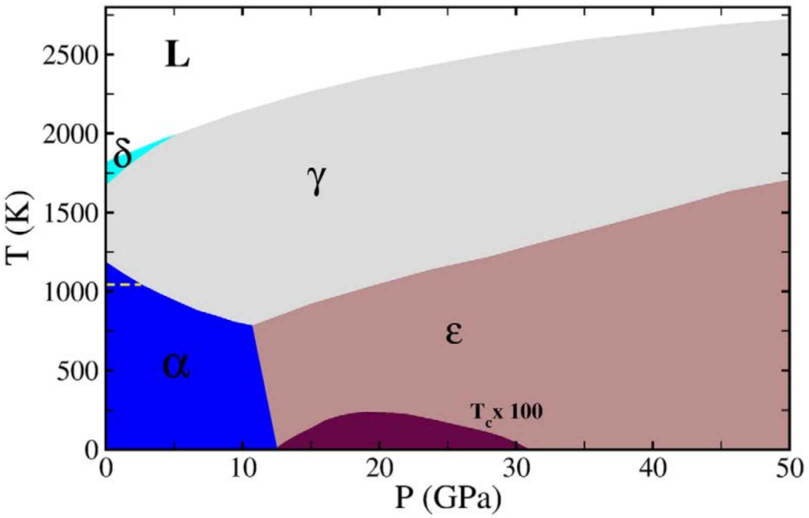


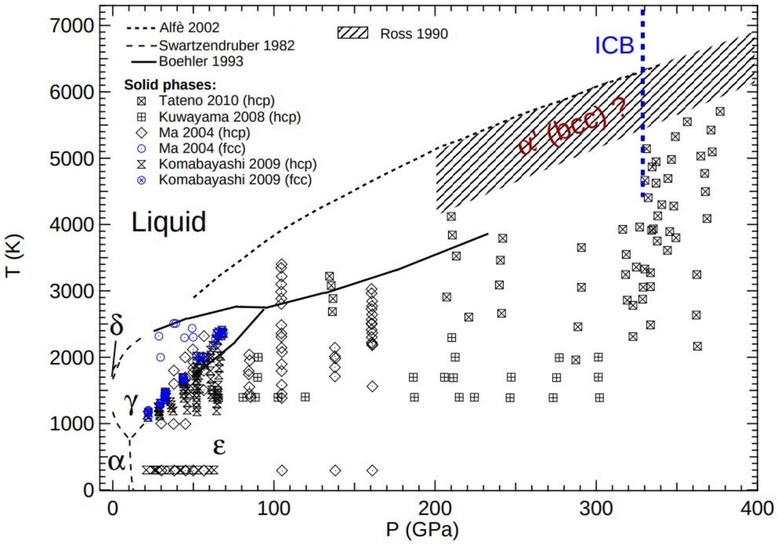


- The outer core, about 2,200 kilometers thick, is mostly composed of liquid iron and nickel. The Ni-Fe alloy of the outer core is very hot, between 4,500° and 5,500° Celsius.
- The inner core is a hot, dense ball of (mostly) iron. It has a radius of about 1,220 kilometers. Temperature in the inner core is about 5,200° Celsius. The pressure is nearly 3.6 million atmosphere.
- Earth's magnetic field is crucial to life on our planet. Although Earth's magnetic field is generally stable, it fluctuates constantly. As the liquid outer core moves, for instance, it can change the location of the magnetic North and South Poles.
- Initially dynamic shock compression and recently Diamond anvil cells are used to simulate the incredibly high pressure at the core.

Nationalgeographic.org; Simone Anzellini - PhD thesis, Université Pierre et Marie Curie

Iron phase diagram





- Geophysically relevant pressure-temperature regime of the Earth's inner core corresponding to the extreme pressure of 360 GPa combined with temperatures up to 6000 K.
- Phases: - α - BCC, ε - HCP, γ - FCC , δ - BCC, α' - BCC?, L - Liquid.

L. V. Pourovskii J. Phys.: Condens. Matter 31 373001 (2019); Simone Anzellini - PhD thesis, Université Pierre et Marie Curie

Linear response theory

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- The linear response of the electronic system to an external, time-dependent perturbation *δv* is given in Fourier space by

$$n_{ind}(q,\omega) = \chi(q,\omega)\delta v(q,\omega)$$

- Compute density-density response function χ(q,ω). Frequently using Kubo-Greenwood formalism, lately using linear-response and real-time TDDFT.

$$\frac{1}{\epsilon(q,\omega)} = 1 + \frac{4\pi}{q^2}\chi(q,\omega)$$

- Compute dynamical electrical conductivity

$$Re[\epsilon(\omega)] = 1 - \frac{1}{\epsilon_0\omega}Im[\sigma(\omega)]$$

$$Im[\epsilon(\omega)] = \frac{1}{\epsilon_0\omega}Re[\sigma(\omega)]$$

- Compute DC conductivity (ω=0) using Drude fit

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}$$

Linear-response TDDFT

- Solving a set of Kohn-Sham equations for the KS orbitals

$$\left[-\frac{1}{2}\nabla_k^2 + V_{\mathrm{S}}(\boldsymbol{r})\right]\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r})$$

- Evaluate Kohn-Sham density-density response function

$$\chi_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega) = \frac{\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega)}{1-\left[V(\boldsymbol{q})+f_{\mathrm{XC}}(\boldsymbol{q},\omega)\right]\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega)}$$

$$\chi^{KS}_{\mathcal{G}\mathcal{G}'}(\boldsymbol{q},\omega) = -\frac{1}{V}\lim_{\eta\to 0^+}\sum_{nm;\boldsymbol{k}}\left[f_{m;\boldsymbol{k}+\boldsymbol{q}}(T)-f_{n;\boldsymbol{k}}(T)\right]$$
$$\times\frac{\langle\psi_{m;\boldsymbol{k}+\boldsymbol{q}}|e^{i(\boldsymbol{q}+\mathcal{G})\boldsymbol{r}}|\psi_{n;\boldsymbol{k}}\rangle\langle\psi_{n;\boldsymbol{k}}|e^{-i(\boldsymbol{q}+\mathcal{G}')\boldsymbol{r}'}|\psi_{m;\boldsymbol{k}+\boldsymbol{q}}\rangle}{\omega-\epsilon_{m;\boldsymbol{k}+\boldsymbol{q}}+\epsilon_{n;\boldsymbol{k}}+i\eta}$$

- $f_{XC}(\mathbf{q}, \omega)$ is the exchange-correlation kernel

$$f_{\mathrm{XC}}(\boldsymbol{q},\omega) = \chi^{KS^{-1}}(\boldsymbol{q},\omega) - \chi^{-1}(\mathbf{q},\omega) - v(\boldsymbol{q})$$

Kubo-Greenwood formula

- The summation over the matrix elements of the Kohn-Sham orbitals with the velocity operator weighted with the difference of the Fermi occupation numbers is performed over all ***N*** bands and ***k***-points.

$$\Re\left[\sigma(\omega)\right] = \frac{2\pi e^2}{3\omega\Omega}\sum_{i,j}^{N}(f_i-f_j)|\langle i|\hat{v}|j\rangle|^2\delta(\epsilon_j-\epsilon_i-\hbar\omega)$$

Real-time TDDFT

- Apply an external electric field ***E***(t) and follow the response of the system with the time evolution of the current density ***j***(t)

$$\vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega) \qquad \mathbf{j}(\mathbf{r},t) = \Im\left[\sum_i^N \phi_i^*(\mathbf{r},t)\nabla\phi_i(\mathbf{r},t)\right] + \frac{1}{c}n(\mathbf{r},t)\,A_{KS}(\mathbf{r},t) \qquad A_{KS}(\mathbf{r},t) = A_{ext}(\mathbf{r},t) + A_{em}(\mathbf{r},t) + A_{xc}(\mathbf{r},t)$$

- Solve Time-dependent Kohn-Sham equation

$$\hat{H}(r,t) = \tfrac{1}{2}\left(-i\nabla + \tfrac{1}{c}A(t)\right)^2 + V_{KS}(r,t)$$

$$\hat{H}(r,t)\phi_{n,k}(r,t) = i\frac{\partial}{\partial t}\phi_{n,k}(r,t)$$

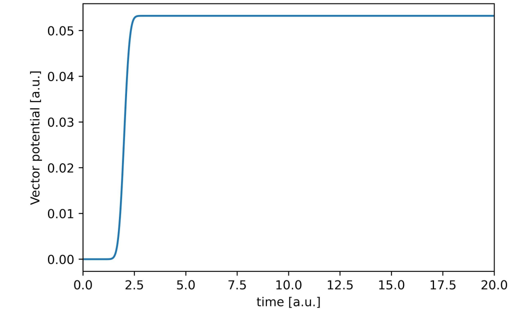
- Fourier transform to obtain the frequency dependent conductivity tensor

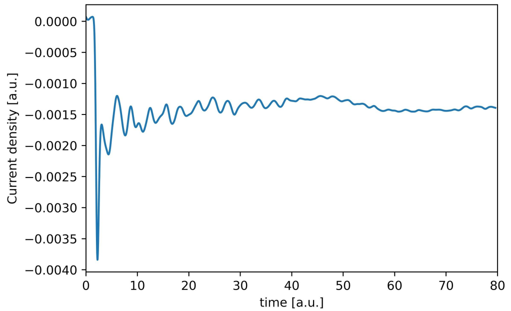
$$\sigma_{ab}(\omega) = \frac{j_a(\omega)}{E_b(\omega)}$$

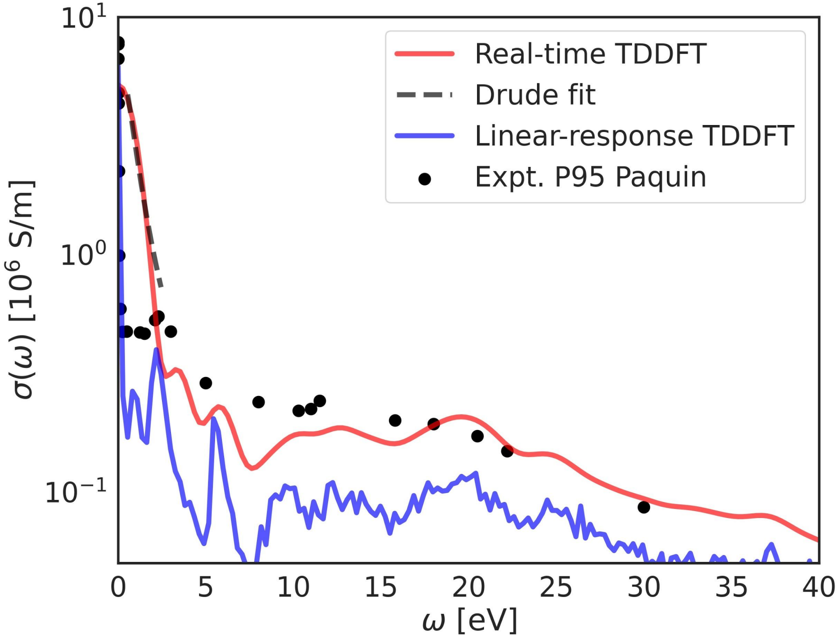
Baczewski et al. PRL 116, 115004 (2016); Andrade et al. Eur. Phys. J. B (2018) 91: 229; Pela et al. arXiv:2102.02630 (2021)

Real-time TDDFT - Ambient Iron

- Sigmoidal pulse in Z direction with a time step=0.02 a.u., 36x36x36 k-points, 60 bands per atom



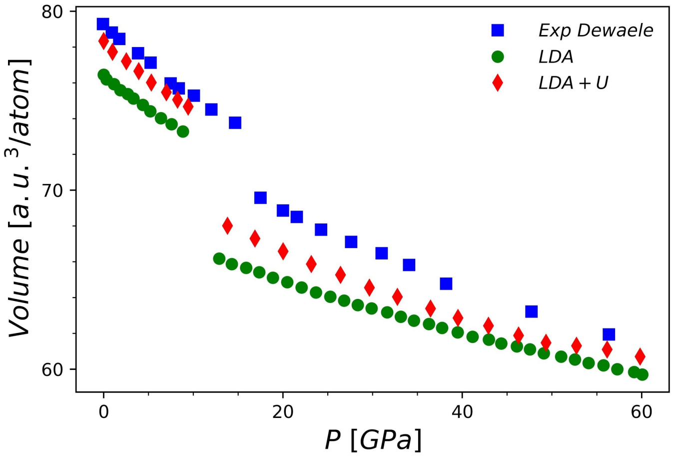




R. A. Paquin - Handbook of optics, Volume II (1995)

Real-time TDDFT - Compressed Iron

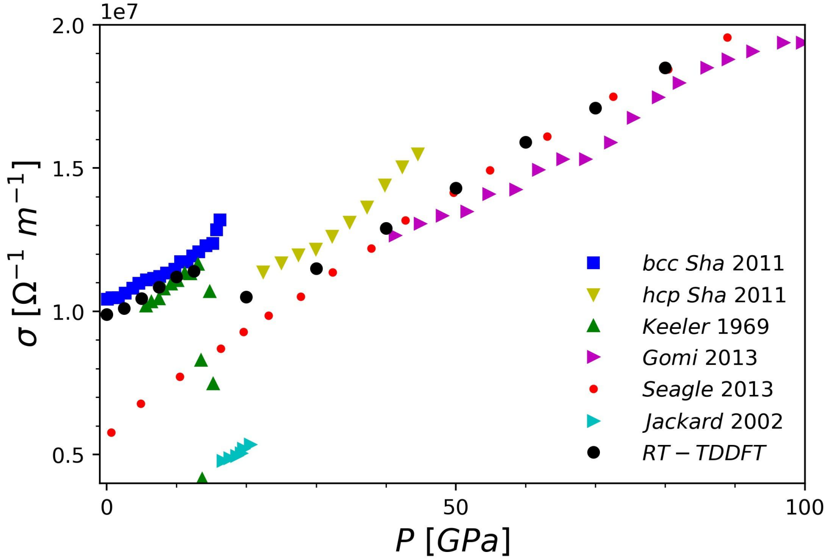
- Phase change around 10-20 GPa from alpha (bcc) to epsilon iron (hcp).
- Electronic correlations in Epsilon iron are important for pressure range up to 60 GPa and at geophysically relevant region of pressure about 360 GPa and temperature of about 6000 K[1].
- Employ DFT+U as on-site Coulomb interactions are particularly strong for localized *d* electrons. U=4.3 eV, J_H=1 eV for epsilon iron[2,3].



[1]L. V Pourovskii J. Phys.: Condens. Matter 31 373001 (2019); [2]MIyake et al. PRB 80, 155134 (2009, [3]L. V. Pourovskii et al. PRB 87, 115130 (2013)

Real-time TDDFT - Compressed Iron

- Phase change around 10-20 GPa from alpha (bcc) to epsilon iron (hcp).
- **Future**: Calculations up to 360 GPa and at higher temperatures.



Sha - J. Phys.: Condens. Matter 23 075401 (2011), Keeler- Solid state communications 7, 271-274 (1969), Gomi - Physics of the Earth and Planetary Interiors 224 88-103 (2013), Seagle - Geo. Research Letters 40 5777-5381 (2013), Jaccard - Phys. Letters A 299 282-286 (2002)

Summary

- The knowledge of the phase diagram and melting curve of iron up to the inner core boundary conditions are of fundamental importance in geophysics and planetary science.
- Electronic correlations are important in certain regimes.
- Real-time TDDFT is capable of describing the natural decay of current in metals, and obtain the frequency dependent conductivity along with the dc value.
- **Future: Simulate relevant higher pressures and temperatures and also study the influence of electronic correlations.**