

# Looking at molecules and solids from a different perspective: **charge density is the key quantity**

- Moving away from the total wavefunction as the key concept: introducing **charge density** as the basic variable
- **Density Functional Theory (DFT)**
  - Energy functional and **Thomas Fermi-Dirac** approximation
  - The **basic theorems** of DFT

# Electronic density

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- The electronic density is the number of electrons *per unit volume* in a given state.

$$\rho(\vec{r}_1) = N \int \dots \int |\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N$$

$\rho$  is a non negative function of three variables,  $x$ ,  $y$ , and  $z$  which integrates to the total number of electrons  $N$

$$\int \rho(\vec{r}) d\vec{r} = N$$

- At any atomic nucleus in an atom, molecule or solid the electron density has a finite value  $\rho(0)$ . In the neighborhood of a nucleus there is always a cusp in the density. **Cusp condition:**

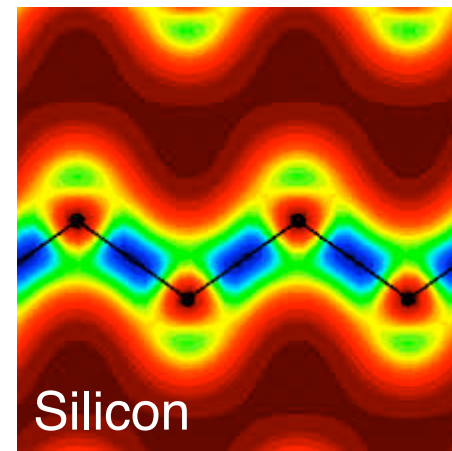
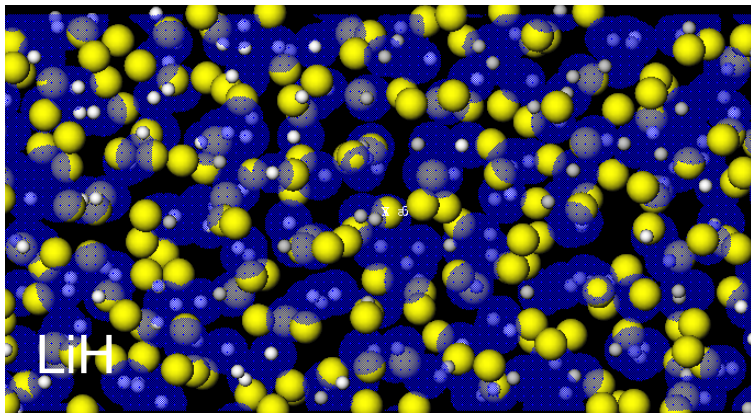
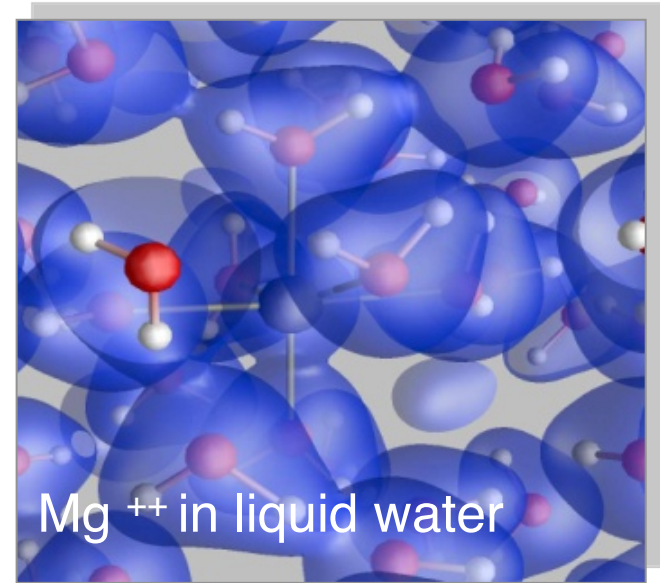
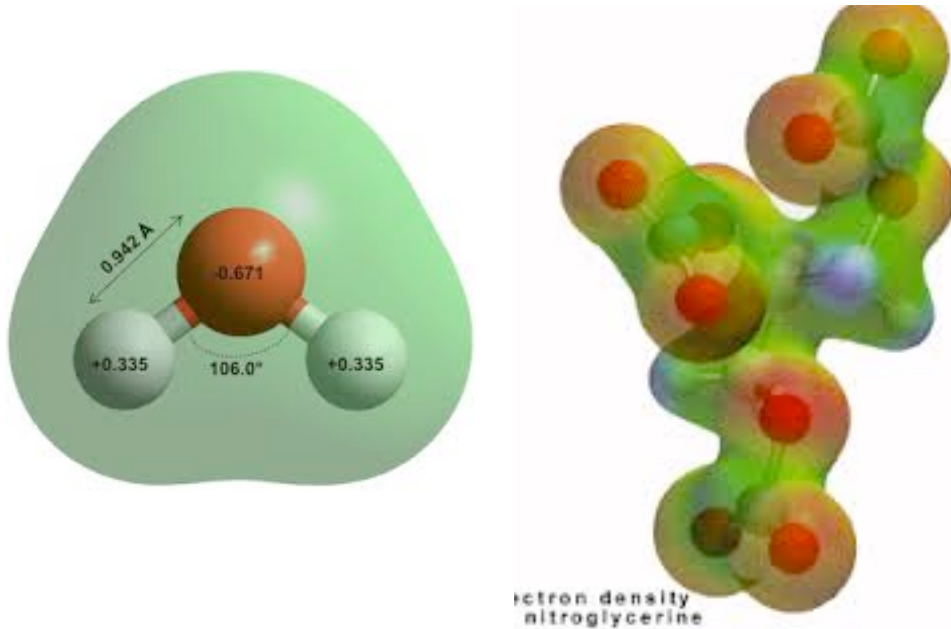
$$\left. \frac{\partial \bar{\rho}(r_\alpha)}{\partial r_\alpha} \right|_{r_\alpha=0} = -2Z_\alpha \bar{\rho}(0) \quad \bar{\rho}(r_\alpha) = \text{spherical average of } \rho(\vec{r}_\alpha)$$

- Long range decay of electronic density in a finite system:

$$\rho \sim \exp \left[ -2 \left( 2 I_{\min} \right)^{1/2} r \right]$$

$\uparrow$  exact 1<sup>st</sup> ioniz. pot.

# Electronic density: molecules, liquids, solids



# Density Functional Theory (DFT) : basic concepts

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- DFT is a theory of **correlated many-body systems**.
- In 1964 Hohenberg and Kohn showed that the **density of particles** in the ground state of a quantum many body system is a **basic variable**, i.e. **all properties** of the system can be considered **unique functionals of the ground state density**.
- In 1965 Mermin **extended DFT** as formulated by Hohenberg and Kohn **to canonical and grand canonical ensembles** (finite T and variable # of particles).
- In 1965 Kohn and Sham formulated **DFT in terms of auxiliary single particles orbitals** and laid the foundation of much of present day methods to treat electrons in atoms, molecules and solids.



1998 Nobel Prize in Chemistry  
to Walter Kohn (left)

# Thomas-Fermi-Dirac approximation

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- The original DFT method for quantum systems goes back to Thomas and Fermi (1927). Although not accurate for present day calculations, the method illustrates the basic ideas of DFT.
  - **Thomas-Fermi** → **approximation for the kinetic energy** as a functional of the density
  - **Thomas-Fermi-Dirac (TFD)** → **addition of exchange-correlation energy functional** to the total energy functional (the Dirac approximation of the exchange functional is still in use today).
  - For the case of equal up and down spins, the TFD functional is:

$$E_{\text{TFD}}[\rho(\vec{r})] = C_1 \int d\vec{r} [\rho(\vec{r})]^{5/3} + \int d\vec{r} v_{\text{ext}}(\vec{r}) \rho(\vec{r}) + C_2 \int d\vec{r} [\rho(\vec{r})]^{4/3} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

$$C_1 = \frac{3}{10} (3\pi^2)^{2/3}; \quad C_2 = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$$

# Thomas-Fermi approximation: the idea of uniform electron distribution

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- Divide space in small cubes (or cells) of side  $l$  and volume  $\Delta V=l^3$ , each containing  $\Delta N$  electrons; assume that in each cell, the electrons behave like independent Fermions at  $T=0$  (cell independent of one another).

- Energy level of a particle in a 3-dim. Infinite well:

$$E(n_x, n_y, n_z) = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2) \equiv \frac{h^2}{8ml^2} \Phi^2; \quad n_x, n_y, n_z = 1, 2, \dots$$

- For large quantum numbers, the # of energy levels with energy smaller than  $\varepsilon$  can be approximated by:  $\Phi(\varepsilon) = \frac{1}{8} \left( \frac{4\pi R^3}{3} \right) = \frac{\pi}{6} \left( \frac{8ml^2\varepsilon}{h^2} \right)^{3/2}$

- The number of energy levels between  $\varepsilon$  and  $\varepsilon + \delta\varepsilon$  is:

$$g(\varepsilon) \Delta\varepsilon = \frac{\pi}{4} \left( \frac{8ml^2}{h^2} \right)^{3/2} \cdot \sqrt{\varepsilon} \delta\varepsilon + O[(\delta\varepsilon)^2]$$

↑ density of states at energy  $\varepsilon$

# Thomas-Fermi approximation: the idea of uniform electron distribution

The probability of state with energy  $\varepsilon$  to be occupied is given by the Fermi-Dirac distribution:

$$f(\varepsilon) = \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} \quad ; \quad f(\varepsilon) = \begin{cases} 1 & \varepsilon < \varepsilon_F \\ 0 & \varepsilon > \varepsilon_F \end{cases} \text{ as } \beta \rightarrow \infty \quad (T \rightarrow 0)$$

$\varepsilon_F$  is the Fermi energy: all states with energy  $\varepsilon$  smaller than  $\varepsilon_F$  are occupied, all those with energy  $\varepsilon$  greater than  $\varepsilon_F$  are empty;  $\varepsilon_F$  is the zero T limit of the chemical potential  $\mu$ .



Enrico Fermi  
(1901-1954)

The energy  $\Delta E$  of electrons in a cell is:

$$\Delta E = 2 \int \varepsilon \cdot f(\varepsilon) g(\varepsilon) d\varepsilon \Rightarrow \Delta E = \frac{8\pi}{5} \left( \frac{2m}{h^2} \right)^{3/2} L^3 (\varepsilon_F)^{5/2}$$

$$\Delta N = 2 \int f(\varepsilon) g(\varepsilon) d\varepsilon = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^{3/2} L^3 (\varepsilon_F)^{3/2}$$

$$\Rightarrow \frac{\Delta E}{\Delta N} = \frac{3}{5} \varepsilon_F$$

# Thomas Fermi approximation for the kinetic energy

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- Adding the contributions of all cells, we find the kinetic energy of an electron gas in the Thomas Fermi approximation:

$$T_{TF} = C_1 \int \rho^{5/3} d\bar{r}$$

Apply *locally* relations appropriate for a homogeneous electronic system

- Here the **kinetic energy is given as a functional of the density**. This is an approximation. Rigorously, the kinetic energy is expressed in terms of the first order density matrix of the electronic system.

$$\rho_1(\bar{r}', \bar{r}) = N \int \dots \int \psi(\bar{r}', s_1, \bar{x}_2, \dots, \bar{x}_N) \psi^*(\bar{r}, s_1, \bar{x}_2, \dots, \bar{x}_N) ds_1 d\bar{x}_2 \dots d\bar{x}_N$$

$$T = \int \left[ -\frac{1}{2} \nabla^2 \rho_1(\bar{r}', \bar{r}) \right]_{\bar{r}=\bar{r}'} d\bar{r}$$



# Thomas Fermi equations

- The ground state energy and density in the TFD approximation can be found by minimizing the functional  $E_{\text{TFD}}$  with respect to all possible  $\rho(\mathbf{r})$  subject to the constraints that the integral of  $\rho(\mathbf{r})$  equals the total # of electrons  $N$ .

$$E_{\text{TFD}}[\rho(\bar{\mathbf{r}})] = C_1 \int d\bar{\mathbf{r}} [\rho(\bar{\mathbf{r}})]^{5/3} + \int d\bar{\mathbf{r}} v_{\text{ext}}(\bar{\mathbf{r}}) \rho(\bar{\mathbf{r}}) + C_2 \int d\bar{\mathbf{r}} [\rho(\bar{\mathbf{r}})]^{4/3} + \frac{1}{2} \int \frac{\rho(\bar{\mathbf{r}}) \rho(\bar{\mathbf{r}}')}{|\bar{\mathbf{r}} - \bar{\mathbf{r}}'|} d\bar{\mathbf{r}} d\bar{\mathbf{r}}'$$

- Unconstrained minimization of the functional

$$\Omega_{\text{TFD}} = E_{\text{TFD}} - \mu \left\{ \int \rho(\bar{\mathbf{r}}) d\bar{\mathbf{r}} - N \right\}$$

yields:

$$\frac{1}{2} (3\pi^2)^{2/3} [\rho(\bar{\mathbf{r}})]^{2/3} + V(\bar{\mathbf{r}}) - \mu = 0$$

Total potential: sum of Hartree, external and exchange-correlation potentials

# Density Functional Theory (DFT) : Hohenberg and Kohn (HK) theorems

- DFT is an **exact** theory of **many body systems**. It is applicable to any system of **interacting particles** in an external potential  $V_{\text{ext}}$ , including electrons within the field of fixed nuclei, where the Hamiltonian is the electronic Hamiltonian we have seen in Lecture 2:

$$\hat{H}_e = \hat{T}_e(r) + \hat{V}_{en}(r) + \hat{V}_{ee}(r) \leftrightarrow \hat{H} = \hat{F} + \hat{V}_{\text{ext}}$$

$\nwarrow$   $V_{\text{ext}}$

$\uparrow$   
 $\hat{F} \equiv \hat{T}_e + \hat{V}_{ee}$

where  $V_{\text{ext}} = V_{\text{eN}}$

**Theorem I (HK-I)** For any system of interacting particles in an external potential  $V_{\text{ext}}$ , the **potential  $V_{\text{ext}}$  is determined uniquely**, except for a constant, **by the ground state particle density  $\rho_0(r)$ .**

**Theorem II (HK-II)** For any external potential  $V_{\text{ext}}$ , the **total energy** of a many body systems of interacting particles is a **unique functional of the density  $\rho(r)$ :  $E=E[\rho(r)]$ .** The exact ground state energy  $E_0$  is the global minimum of this functional and the density  $\rho(r)$  which minimizes the functional is the ground state energy  $\rho_0(r)$ .

$$\begin{array}{ccc}
 V_{\text{ext}}(\bar{r}) & \Leftarrow & \rho_0(\bar{r}) \\
 \Downarrow & & \Uparrow \\
 \psi_i(\{\bar{r}\}) & \Rightarrow & \psi_0(\{\bar{r}\})
 \end{array}$$

**HK-I: the potential  $V_{\text{ext}}$  is determined *uniquely*, except for a constant, by the ground state particle density  $\rho_0(\mathbf{r})$ .**

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Proof by *reductio ad absurdum*: assume that a second different external potential  $V'_{\text{ext}}(\mathbf{r})$  with ground-state  $|\Psi'_0\rangle$  gives rise to the same density  $\rho(\mathbf{r})$ . The ground-state energies are  $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$  and  $E'_0 = \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle$  where  $\hat{H} = \hat{F} + \hat{V}_{\text{ext}}$  and  $\hat{H}' = \hat{F} + \hat{V}'_{\text{ext}}$ . Taking  $|\Psi'_0\rangle$  as a trial wave-function for the Hamiltonian  $\hat{H}$ , we obtain the strict inequality

$$\begin{aligned} E_0 &< \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \langle \Psi'_0 | (\hat{H} - \hat{H}') | \Psi'_0 \rangle \\ &= E'_0 + \int d\mathbf{r} \rho(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})], \end{aligned}$$

whereas taking  $|\Psi_0\rangle$  as a trial wave-function for  $\hat{H}'$  gives

$$\begin{aligned} E'_0 &< \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | (\hat{H}' - \hat{H}) | \Psi_0 \rangle \\ &= E_0 - \int d\mathbf{r} \rho(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] \end{aligned}$$

and adding these two equations together results in the contradiction

$$E_0 + E'_0 < E_0 + E'_0.$$

**HK-I: the potential  $V_{\text{ext}}$  is determined *uniquely*, except for a constant, by the ground state particle density  $\rho_0(\mathbf{r})$ .**

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Since the ground state density uniquely determines the external potential, the Hamiltonian is fully determined, except for a constant shift of the energy, by the ground state charge density.



The many body wavefunctions for all states (ground and excited) are fully determined



**All properties of the system are completely determined only by the ground state density  $\rho_0(\mathbf{r})$ .**

# HK-II: the **total energy** of a many body systems of interacting particles is a **unique functional of the density** $\rho(\mathbf{r})$ : $E=E[\rho(\mathbf{r})]$ .

So for all densities  $\rho(\mathbf{r})$  which are ground-state densities for some external potential ( $\rho$ -representable) the functional  $F[\rho] = \langle \Psi | \hat{H} | \Psi \rangle$  is unique and well-defined, since  $\rho(\mathbf{r})$  determines the external potential and  $N$  (and therefore  $\hat{H}$ ) and thence  $|\Psi\rangle$ . Now a functional for an arbitrary external potential  $V(\mathbf{r})$  unrelated to the  $V_{\text{ext}}(\mathbf{r})$  determined by  $\rho(\mathbf{r})$  can be defined:

$$E_V[\rho] = F[\rho] + \int d\mathbf{r} V(\mathbf{r})\rho(\mathbf{r}).$$

For all  $\rho$ -representable densities  $\rho(\mathbf{r})$ ,  $E_V[\rho] \geq E_0$  where  $E_0$  is now the ground-state energy for  $N$  electrons in the external potential  $V(\mathbf{r})$ .

Proof of this energy variational principle: by the first theorem, a given  $\rho(\mathbf{r})$  determines its own external potential  $V_{\text{ext}}(\mathbf{r})$  and ground-state  $|\Psi\rangle$ . If this state is used as a trial state for the Hamiltonian with external potential  $V(\mathbf{r})$ , we have

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{V} | \Psi \rangle = F[\rho] + \int d\mathbf{r} V(\mathbf{r})\rho(\mathbf{r}) = E_V[\rho] \geq E_0$$

by the variational principle. For non-degenerate ground-states, equality only holds if  $|\Psi\rangle$  is the ground-state for potential  $V(\mathbf{r})$ .

$F[\rho]$  is a unique, unknown functional of the density.

**The functional  $E[\rho]$  alone is sufficient to determine the ground state energy and density.** In general, the excited states of the electrons must be determined by other means.

# The constrained search formulation of DFT

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**Levy's formulation:** we define a functional of the density  $\rho(\mathbf{r})$  for the operator  $\hat{F}$

$$F[\rho] = \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \hat{F} | \Psi \rangle$$

i.e. the functional takes the minimum value of the expectation value with respect to all states  $|\Psi\rangle$  which give the density  $\rho(\mathbf{r})$ . For a system with external potential  $V(\mathbf{r})$  and ground-state  $|\Psi_0\rangle$  with energy  $E_0$ , consider a state  $|\Psi[\rho]\rangle$ , an  $N$ -electron state which yields density  $\rho(\mathbf{r})$  and minimises  $F[\rho]$ . Define  $E_V[\rho]$  as:

$$E_V[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V(\mathbf{r}) = \langle \Psi[\rho] | (\hat{F} + \hat{V}) | \Psi[\rho] \rangle$$

but since  $\hat{H} = \hat{F} + \hat{V}$ , by the variational principle we obtain

$$E_V[\rho] \geq E_0$$

# The constrained search formulation for DFT

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with equality only if  $|\Psi_{[\rho]}\rangle = |\Psi_0\rangle$ . This holds for all densities which can be obtained from an  $N$ -electron wave-function ( $N$ -representable). But from the definition of  $F[\rho]$  we must also have

$$F[\rho_0] \leq \langle \Psi_0 | \hat{F} | \Psi_0 \rangle$$

since  $|\Psi_0\rangle$  must be one of states which yields  $\rho_0(\mathbf{r})$ . Adding  $\int d\mathbf{r} \rho_0(\mathbf{r}) V(\mathbf{r})$  gives

$$E_V[\rho_0] \leq E_0$$

$$\Rightarrow E_V[\rho_0] = E_0$$

Thus the ground-state density  $\rho_0(\mathbf{r})$  minimises the functional  $E_V[\rho]$  and the minimum value is the ground-state electronic energy.

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# From an energy functional of the charge density to Schroedinger-like equations for single particle orbitals

- We moved away from the total wavefunction as the key concept and introduced the **charge density** as the basic variable → **Density Functional Theory (DFT)**
- We now go back to wavefunctions but NOT to many body wavefunctions; we introduce **AUXILIARY single particle orbitals** → **Kohn-Sham formulation of DFT**



# Density Functional Theory (DFT) : basic concepts

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- DFT is a theory of **correlated many-body systems**.
- In 1964 Hohenberg and Kohn showed that the **density of particles** in the ground state of a quantum many body system is a **basic variable**, i.e. **all properties** of the system can be considered **unique functionals of the ground state density**.

$$E_{HK}[\rho] = F_{HK}[\rho] + \int d\vec{r} V_{\text{ext}}(\vec{r}) \rho(\vec{r})$$

- In 1965 Kohn and Sham formulated **DFT in terms of auxiliary single particles orbitals** and laid the foundation of much of present day methods to treat electrons in atoms, molecules and solids.

# HK formulation of Density Functional Theory

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$$E_{\text{HK}}[\rho] = F_{\text{HK}}[\rho] + \int d\vec{r} V_{\text{ext}}(\vec{r}) \rho(\vec{r})$$

- The functional  $F[\rho]$  is unknown; it includes all internal, kinetic and potential energies of the interacting electron system:

$$F = T[\rho] + E_{\text{int}}[\rho]$$

- No one has found a *practical* way to extract from the density any general set of properties, e.g. whether a material is a metal or an insulator.
- There is no known way to go from the density to the kinetic energy  $T[\rho]$

# The Kohn-Sham (KS) formulation of Density Functional Theory

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L. Sham, UC San Diego

- The KS approach to DFT consists in replacing the difficult interacting many-body system described by the Hamiltonian  $H$  and functional  $E_{HK}$  with a different *auxiliary system that can be solved more easily*.
- The *ansatz* of Kohn-Sham assumes that the ground state density of the original many-body system is equal to that of *some chosen non-interacting system which can be exactly soluble by numerical means*. All the difficult many-body terms are incorporated into an *exchange-correlation functional of the density*.

# The Kohn-Sham ansatz: two assumptions

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- Given an **interacting many body system**, there exist an **non-interacting auxiliary system** whose ground state density is the same as that of the interacting many body system. In other words: the **exact ground state density**  $\rho_0$  of an interacting many body system can be represented by the **ground state density of an auxiliary system of non-interacting particles**. There is no rigorous proof of the existence of such an auxiliary system for most molecules and materials.

- The auxiliary Hamiltonian is chosen to be:  $\hat{H}_{aux.}^{\sigma} = -\frac{1}{2} \nabla^2 + V_{eff}^{\sigma}(\vec{r})$   
where  $V_{eff}^{\sigma}(\vec{r})$  is a **local** potential.

(The assumption that  $V$  is local is not essential)

# The Kohn-Sham ansatz: the *auxiliary* system

- The density of the auxiliary system is given by:

$$\rho(\vec{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\psi_i^{\sigma}(\vec{r})|^2$$

Independent particle wavefunctions

- The independent particle kinetic energy is:

$$T_s = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\vec{r} |\nabla \psi_i^{\sigma}(\vec{r})|^2$$

- We define the classical Coulomb interaction energy of the electron density interacting with itself:

$$E_{\text{Hartree}}[\rho] = \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

- The KS approach to DFT is to rewrite the HK expression for the ground state energy functional as:

$$E_{\text{KS}} = T_s[\rho] + \int d\vec{r} V_{\text{ext}}(\vec{r})\rho(\vec{r}) + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho]$$

# The Kohn-Sham ansatz: the *auxiliary* system

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$$E_{KS} = T_s[\rho] + \int d\vec{r} V_{\text{ext}}(\vec{r})\rho(\vec{r}) + E_{\text{Hartree}}[\rho] + E_{xc}[\rho]$$

• **All many body effects of exchange and correlation are grouped into the exchange and correlation energy  $E_{xc}[\rho]$ .** If the universal functional  $E_{xc}$  were known, the exact ground state energy and density of the auxiliary system and then of the corresponding many-body system could be found by minimizing  $E_{KS}$  with respect to the density.

•  $E_{xc}$  is not known and in practice **approximate forms are used**.

# The Kohn Sham equations

- Minimize  $E_{KS}$  with respect to the density; since  $T_s$  is given in terms of single particle orbitals, we proceed as follow to minimize  $E_{KS}$

$$\frac{\delta E_{KS}}{\delta \psi_i^*(\vec{r})} = \frac{\delta T_s}{\delta \psi_i^*} + \left[ \frac{\delta E_{ext}}{\delta \rho(\vec{r})} + \frac{\delta E_{Hartree}}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}}{\delta \rho(\vec{r})} \right] \cdot \frac{\delta \rho(\vec{r})}{\delta \psi_i^*(\vec{r})} = 0$$

with:  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

$$H_{KS} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad \text{with } H_{KS}(\vec{r}) = -\frac{1}{2} \nabla^2 + V_{KS}(\vec{r})$$

**Kohn-Sham equations**

**Kohn-Sham potential:** it depends on  $\rho$  and needs to be determined self-consistently.

$$V_{KS} = V_{ext} + \frac{\delta E_{Hartree}}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}}{\delta \rho(\vec{r})} \equiv V_{ext} + V_{Hartree} + V_{xc}(\vec{r})$$

# Meaning of eigenvalues in the KS equations

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$$H_{KS} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

- The eigenvalues are NOT the energies to add or subtract electrons from the interacting many body system. One exception is the highest eigenvalue in a finite system (e.g. an atom or a molecule) which equals the negative of the first ionization potential.
- The eigenvalues have a definite mathematical meaning:

$$\epsilon_i = \frac{d E_{TOT}}{d f_i} = \int d\vec{r} \frac{d E_{TOT}}{d \rho(\vec{r})} \cdot \frac{d \rho(\vec{r})}{d f_i}$$

where  $f_i$  are occupation numbers for the single particle wavefunctions  $\psi_i$ .



# Exchange correlation potential

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- Having separated explicitly the independent particle kinetic energy and the long range Hartree terms, the remaining  $E_{xc}$  can be *reasonably* approximated as a local or nearly local functional of the density

$$E_{xc} = \int d\bar{r} \rho(\bar{r}) \epsilon_{xc}(\rho(\bar{r}); \bar{r})$$

where  $\epsilon_{xc}$  is an energy per electron at point  $r$  and it depends only upon the density  $\rho(r)$  in some neighborhood of  $r$ .  $\epsilon_{xc}$  is *not* uniquely defined by the integral above.

- $V_{xc}$  is the functional derivative of  $E_{xc}$  and it is a functional of the density:

$$V_{xc}(\bar{r}) = \epsilon_{xc}(\rho(\bar{r}); \bar{r}) + \rho(\bar{r}) \frac{\delta \epsilon_{xc}}{\delta \rho(\bar{r})}$$

# The local density approximation

- The exchange correlation density  $\epsilon_{xc}$  is assumed to be the same as that of a **homogeneous electron gas** with that density.

$$E_{xc}^{LDA} = \int d\vec{r} \rho(\vec{r}) \epsilon_{xc}^{hom.}(\rho(\vec{r}))$$

$$\epsilon_{xc}^{hom.} = \epsilon_x^{hom.} + \epsilon_c^{hom.} = -\frac{3}{4} \left( \frac{6}{\pi} \rho(\vec{r}) \right)^{1/3} + \epsilon_c^{hom.}$$

For a spin polarized system, the exchange energy of a homogeneous electron gas is given by:

$$\epsilon_x^{hom}(\rho, \xi) = \epsilon_x(\rho, 0) + [\epsilon_x(\rho, 1) - \epsilon_x(\rho, 0)] f_x(\xi)$$

$$\xi = \frac{\rho^\uparrow - \rho^\downarrow}{\rho}$$

$$f_x(\xi) = \frac{1}{2} \frac{(1+\xi)^{4/3} + (1-\xi)^{4/3} - 2}{2^{1/3} - 1}$$

From Quantum Monte Carlo calculations

# The correlation energy of the homogeneous electron gas

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The correlation energy has been obtained by Quantum Monte Carlo calculations (Ceperley and Alder, Phys Rev Lett. 1980) and parametrized as a function of density (or  $r_s$ )

$$e_C^{hom}(\rho) = \begin{cases} -0.1423(1 + 1.0529\sqrt{r_s} + 0.3334r_s)^{-1} & \text{if } r_s \geq 1, \\ -0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.002 r_s \ln r_s & \text{if } r_s < 1. \end{cases}$$

$r_s := (4\pi\rho/3)^{-1/3}$  Wigner-Seitz radius  
[see, e.g. Perdew & Zunger, PRB **23** 5048 (1981)]

We now have an *ab-initio*, approximate DFT which can be used in practice to compute properties of molecules and condensed systems.

The basic variable: electronic charge density

$$\rho = \sum_{i=1}^N |\psi_i(\vec{r})|^2 \quad \text{with} \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

The total energy in terms of the charge density and the single particle orbitals

$$E_{KS} = -\frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\vec{r}) \nabla^2 \psi_i(\vec{r}) d\vec{r} + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + \int d\vec{r} \rho(\vec{r}) \epsilon_{xc}(\rho) + \int d\vec{r} V_{\text{ext}}(\vec{r}) \rho(\vec{r})$$

The Kohn-Sham equations: set of N non linear differential equations for the single particles orbitals; the potential  $V_{KS}$  depends '*self-consistently*' upon the charge density

$$\left( -\frac{1}{2} \nabla^2 + V_{KS}[\rho(\vec{r})] \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad \text{with} \quad V_{KS} = \frac{\delta E_{KS}}{\delta \rho(\vec{r})}$$

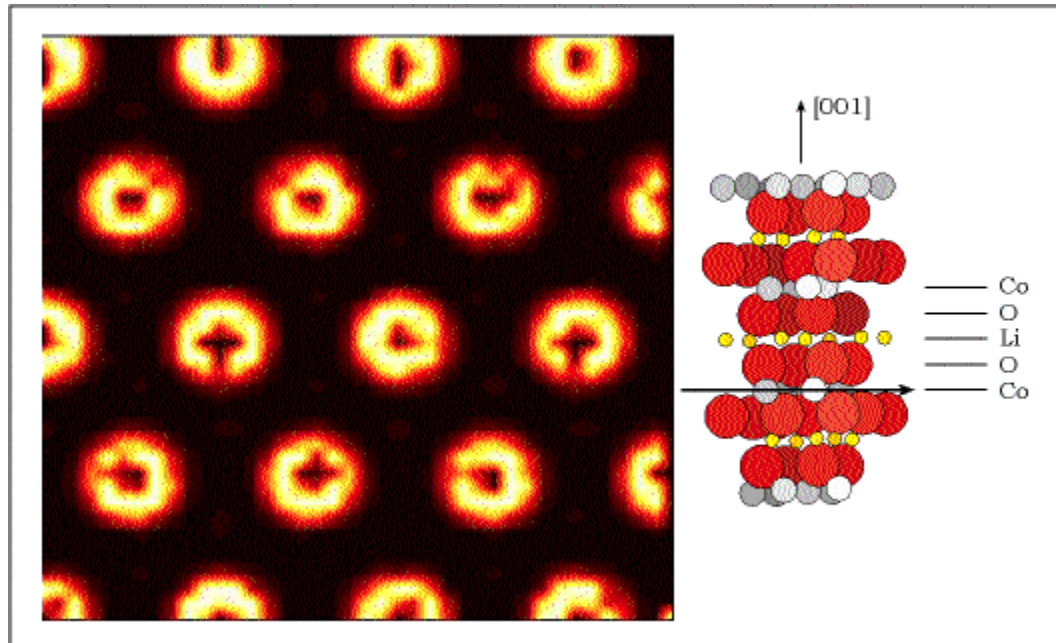
The LDA approximation: approximation for the exchange correlation energy density

$$\epsilon_{xc} \sim \epsilon_{xc}^{\text{hom}} = \epsilon_x^{\text{hom}} + \epsilon_c^{\text{hom}}$$

$\epsilon_x^{\text{hom}}$  is known exactly;  $\epsilon_{xc}$  and  $E_{xc}[\rho]$  are in general unknown.

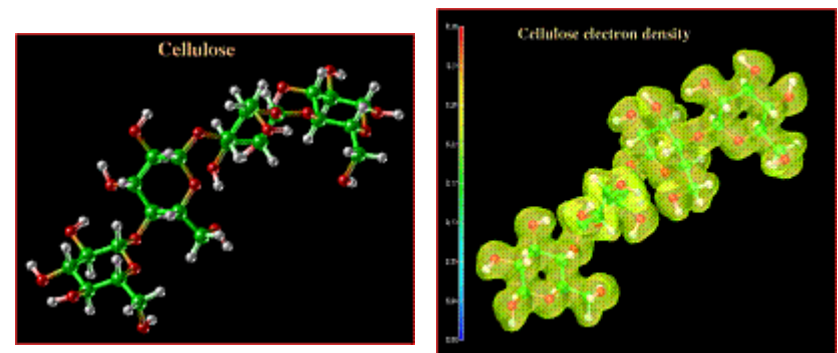
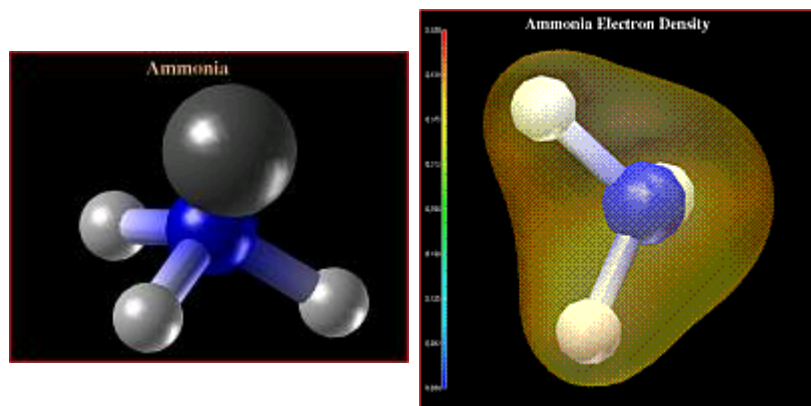
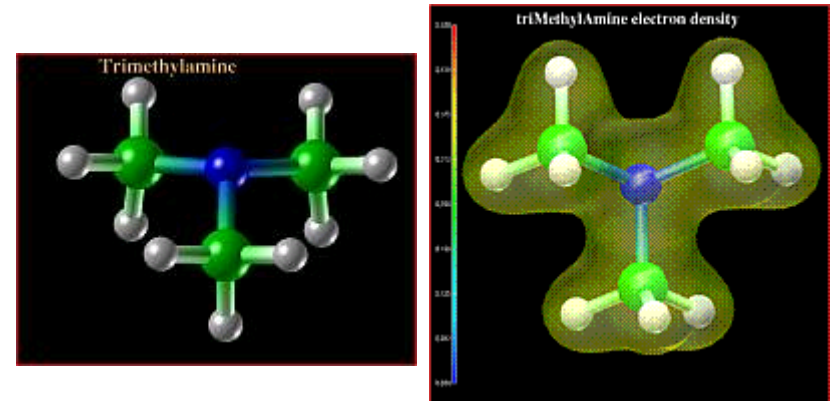
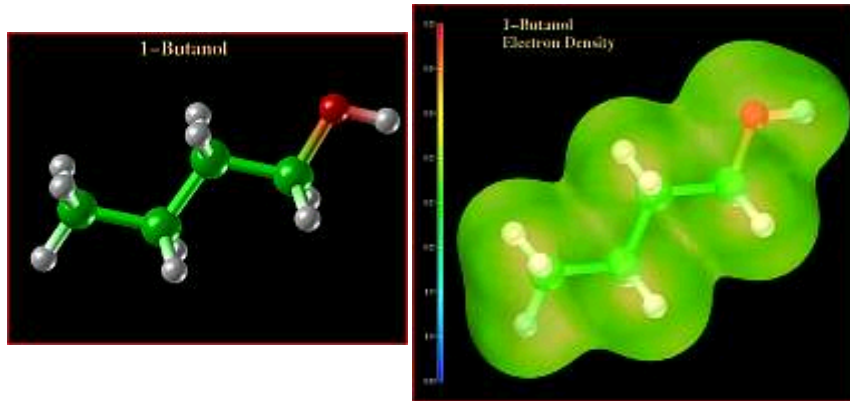
# Charge density in a layered solid: $\text{LiCoO}_2$

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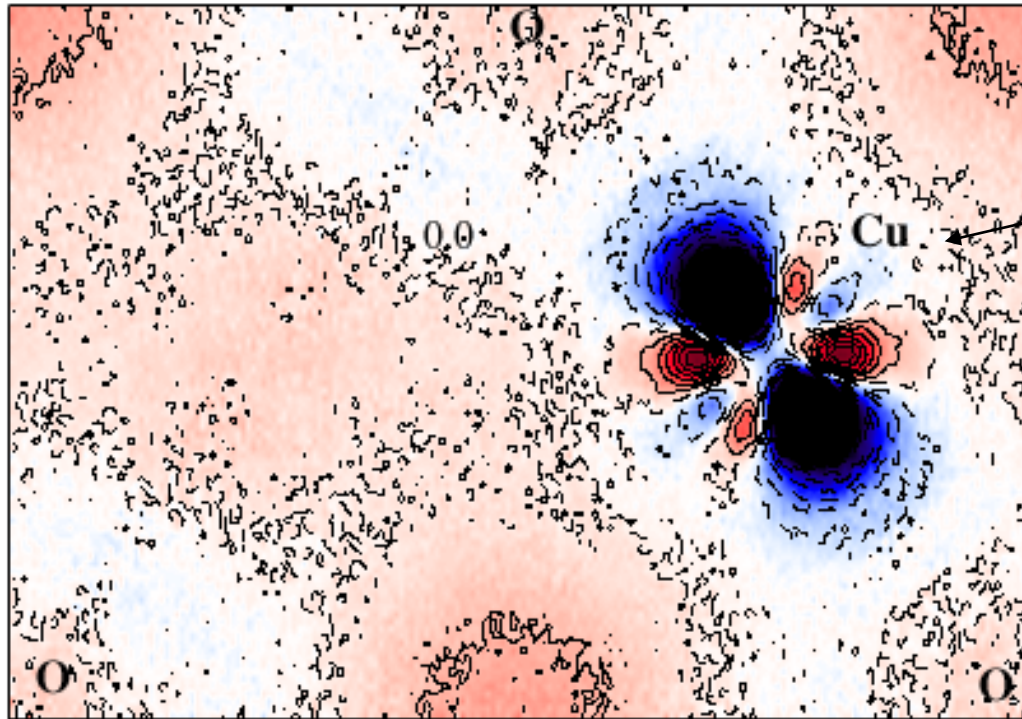
From G.Ceder

# Charge densities in molecules



# Electronic charge density in solids

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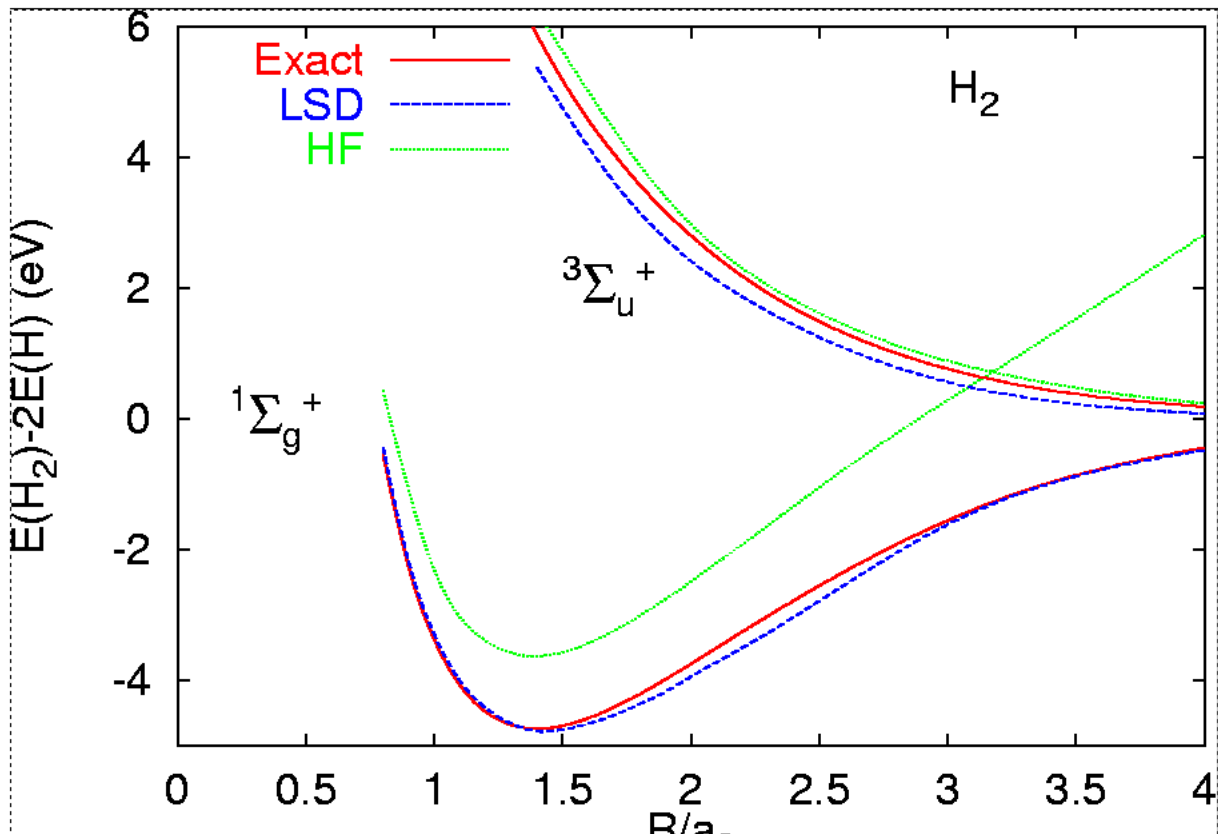


d orbitals

Electron density in  $\text{La}_2\text{CuO}_4$  - difference from sum of atom densities – from J. M. Zuo (UIUC)

# The Hydrogen molecule

- Hydrogen molecules - using the LSDA  
(from O.Gunnarson)





# Phase transformations in crystalline Si and Ge

• from Yin and Cohen (1982)

Needs and Mujica (1995)

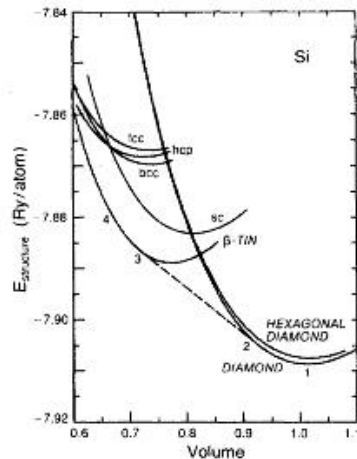


FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to  $\Omega_{\text{expt}}$  (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the  $\beta$ -tin phase ( $c/a=0.552$ ).

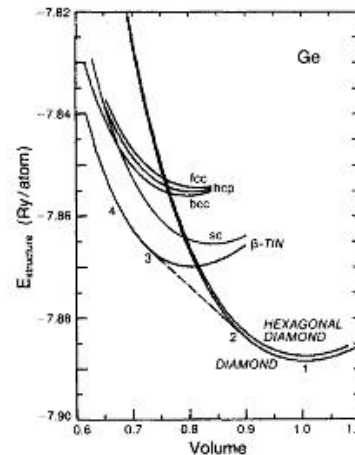


FIG. 6. Total-energy curves of the seven phases of Ge as a function of the atomic volume normalized to  $\Omega_{\text{expt}}$  (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the  $\beta$ -tin phase ( $c/a=0.551$ ).

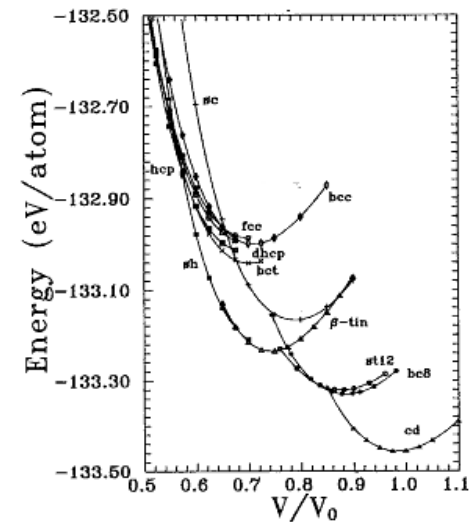


FIG. 1. The energy  $E$  in eV per atom vs the volume  $V$  for the 11 phases under consideration. The volume is given in terms of the reduced volume  $V/V_0^{\text{exp}}$ , where  $V_0^{\text{exp}}=20.024 \text{ \AA}^3$  per atom is the experimental equilibrium volume of cd-Si. The different symbols indicate our theoretical values, and the lines are fits to these data.