Local Density Functional Theory: Basics and its Applications

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Contents

1. Why the density fuctional theory?

- One-particle Schrodinger's equation:

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right]\psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

where the eigenstate can be represented by

$$\psi_n(\mathbf{r}) = \sum_{\alpha=1}^{M} c_n(\alpha)\phi_\alpha(\mathbf{r})$$

- N-particle Schrodinger's equation:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v(\mathbf{r_i}) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi_n(\{\mathbf{r}_i\}) = E_n \Psi_n(\{\mathbf{r}_i\})$$

where the N-particle state can be represented by

$$\Psi_n(\{\mathbf{r}_i\}) = \sum_{\{\alpha_i\}} C_n(\{\alpha_i\})\Phi_{\{\alpha_i\}}(\{\mathbf{r}_i\})$$

Note that $\Phi_{\{\alpha_i\}}$ can be a state corresponding to the Slater determinant of $\{\phi_{\alpha_i}(\mathbf{r}_i)\}$.

- Suppose that $\alpha_i = 1, ..., M$ for the i-th particle residing at the independent lattice site. Then, the total number of available states $\{\Phi_{\{\alpha_i\}}\}$ becomes $N^M \to N!$.

$N!$-dimensional space vs. 3d-functional space

$N^M \times N^M$ matrix vs. $M \times M$ matrix

Hohenberg-Kohn Theorem

- The exact many-body wavefunction (and all the ground state properties) of the interacting many-body system is determined by the charge density $n(\mathbf{r})$
- There exists a unique universal functional of the density, $F[n(\mathbf{r})]$, independent of the external potential $v(\mathbf{r})$, such that

$$E_v = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$$

has its minimum value at the correct ground-state energy associated with $v(\mathbf{r})$.

$$n(\mathbf{r}) = \langle \Psi_o | \hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}) | \Psi_o \rangle \Leftrightarrow |\Psi_o\rangle$$

Example: free electrons in a box with a constant potential v_o

- Fermi Energy: $\varepsilon_F = k_F^2/2 + v_o$
- Fermi wave vector: $k_F = \sqrt{2(\varepsilon_F - v_o)}$
- Number density:

$$n = \frac{k_F^3}{3\pi^2}$$

$$n(\mathbf{r}) = n(v_o) = \frac{1}{3\pi^2}\left(2(\varepsilon_F - v_o)\right)^{3/2}$$

- Total energy:

$$\frac{E_o}{V} = \frac{3}{5}\frac{k_F^2}{2}n + v_o n = \frac{3}{10}(3\pi^2)^{2/3}n^{5/3} + v_o n$$

Note: Total energy E_o is a function of n, which is in turn a function of v_o.

Thomas-Fermi Theory

Description of Kinetic Energy for inhomogeneous systems as a function of local density $n(\mathbf{r})$:

$$T = \frac{3}{10}(3\pi^2)^{2/3} \int [n(\mathbf{r})]^{5/3} d\mathbf{r}$$

Example: interacting electrons in a box with a constant potential $v_o = 0$

For a large density system, i.e., $n \gg 1$, the total energy of the interacting electron gas can be expressed in a perturbation expansion of the parameter $(1/k_F) \propto (1/n^{1/3})$:

$$\begin{aligned} E &= E_o(1 + A\frac{1}{k_F} + B\frac{1}{k_F^2} + ...) \\ &= T_o - A'n^{4/3} + B'n + C'\ln(n) + ... \end{aligned}$$

- T_o : kinetic energy
- $E_x = -A'n^{4/3}$: exchange energy
- $E_c = B'n + C'\ln(n) + ...$: correlation energy

The form of the E_{xc} exchange-correlation energy is known precisely only for the homogeneous interacting electron gas (jellium) system.

Comparison of Energy Contributions from Kinetic, Hartree, ...

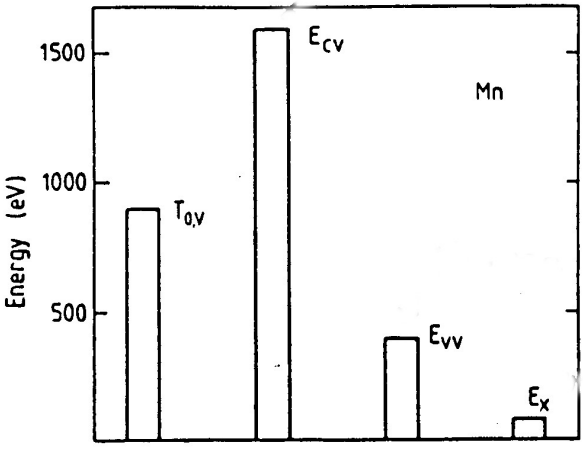


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

- **Slater**'s X-α Method

$$E = \frac{3}{10}(3\pi^2)^{2/3}\int [n(\mathbf{r})]^{5/3} d\mathbf{r} - 2\alpha C \int [n(\mathbf{r})/2]^{4/3} d\mathbf{r}$$

  - For jellium, $\alpha C = 3(3/4\pi)^{1/3}$.
  - For the real system, α is adopted as an empirical parameter.

- Kohn-Sham Form of Exchange Energy

$$v_x(n) = \frac{dE_{xc}(n)}{dn} = \frac{4}{3}C\frac{1}{2^{1/3}}n^{1/3}$$

- Wigner Form of Exchange-Correlation Energy

$$E_{xc} = E_x + E_c, \quad \text{with} \quad E_c = \frac{-0.88}{r_s + 7.8}\text{Ryd}$$

- Hedin-Lundqvist Form of E_{xc}: RPA for jellium

- Ceperley-Alder Form parameterized by Perdew and Zunger:

  Nearly Exact Quantum Monte Carlo Calculations on jellium

2. Exchange-Correlation Energy

- The presence of an exchange-correlation hole, as discussed by Gnnarsson and Lundqvist, is a key point as to why the local density approximation works so well.
- There is a sum rule on the hole in a metal.
- Only the spherical average is needed for the total energy.

Exchange-Correlation Hole

$$E_C = \int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Two particle density $n_2(\mathbf{r}_1, \mathbf{r}_2)$:

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} n(\mathbf{r}_1) n(\mathbf{r}_2) [1 + g(\mathbf{r}_1, \mathbf{r}_2)]$$

Pair correlation function: $g(\mathbf{r}_1, \mathbf{r}_2)$

Exchange-correlation hole:

$$n_{xc}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2)$$

where there exists a sum rule:

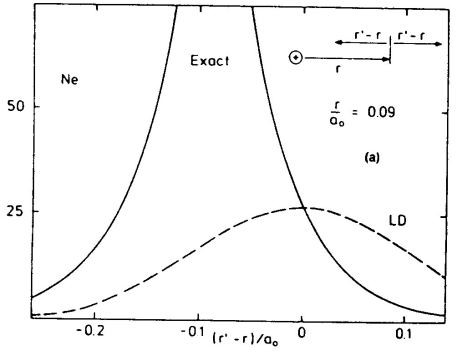
$$\int n_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int n(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$$

- Hatree term:

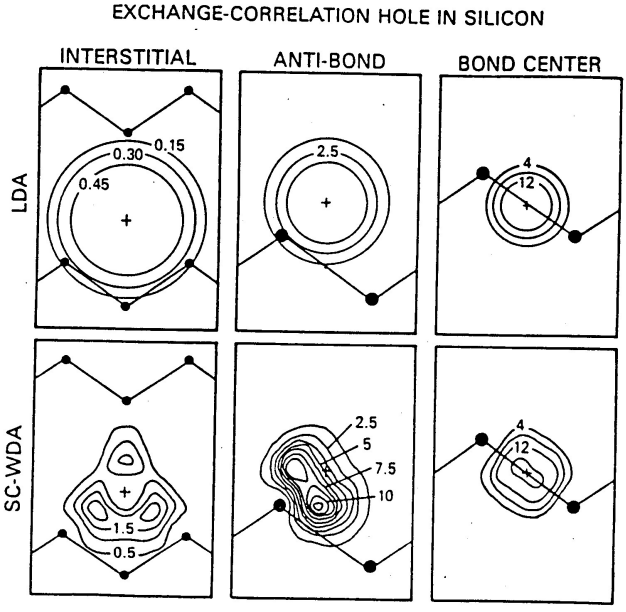
$$E_H = \frac{1}{2}\int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n(\mathbf{r}_1) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- Exchange-correlation term:

$$E_{xc} = \frac{1}{2}\int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n(\mathbf{r}_1) n_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$



Exchage-Correlation Holes in Si



3. Kohn-Sham Equation

Finding "$n(\mathbf{r})$" for the ground state?

Applying the variational method for the minimum $E_v[n]$ under the contraint $\int n(\mathbf{r})d\mathbf{r} = N$:

$$\frac{\delta}{\delta n(\mathbf{r})}\left[E_v - \mu\left(\int n(\mathbf{r})d\mathbf{r} - N\right)\right] = 0$$

$$\frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu$$

N-representability

Introducing a new set of extra variational "parameters" $\{\phi_i(\mathbf{r})|i = 1, 2, ..., N\}$ for the density $n(\mathbf{r})$:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

$\phi_i(\mathbf{r})$ ($i = 1, ..., N$) are the orbitals of **fictitious** (non-interacting fermion) N-particles moving under the **effective** potential v_{eff}:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

With the number-of-particles constraint:

$$\int |\phi_i(\mathbf{r})|^2 d\mathbf{r} = 1$$

the total energy functional can be written by

$$E_v[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{ion}$$

$$T_s[n] = -\frac{1}{2}\sum_{i=1}^{N}\langle\phi_i|\nabla^2|\phi_i\rangle$$

$$E_H[n] = \frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$E_{xc}[n] = \int \varepsilon_{xc}[n]n(\mathbf{r})d\mathbf{r}$$

$$E_{ion} = \frac{1}{2}\sum_{ij}\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Taking the **variation** with respect to $\phi_i(\mathbf{r})$:

$$\frac{\delta}{\delta\phi_i^*(\mathbf{r})}\left[E_v[n] - \sum_{i=1}^{N}\epsilon_i\left(\int|\phi_i(\mathbf{r})|^2 d\mathbf{r} - 1\right)\right] = 0$$

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int\frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + v_{xc}(\mathbf{r})$$

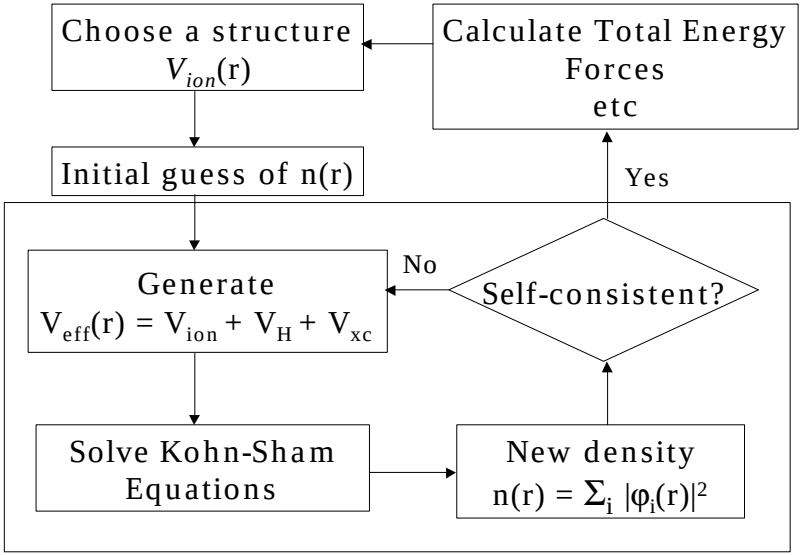
Local Density Approximation

Assuming $\varepsilon_{xc}[n] = \varepsilon_{xc}(n(\mathbf{r}))$,

$$v_{xc}(\mathbf{r}) = \frac{d}{dn(\mathbf{r})}\left(n\varepsilon_{xc}(n(\mathbf{r}))\right)$$

The n-dependence of ε_{xc} can be obtained as accurately as possible via Quantum Monte Carlo Calculations of Ceperley-Alder Form parameterized by Perdew and Zunger.

Self-Consistent Calculation Algorithm



4. Total Energy Calculations

$$
\begin{aligned}
E_{tot} &= \sum_{i=1}^{N} \epsilon_i \\
&- \frac{1}{2} \int \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n(\mathbf{r}_1) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&+ \int n(\mathbf{r}) [\varepsilon_{xc}(n) - v_{xc}(n)] d\mathbf{r} \\
&+ E_{ion}
\end{aligned}
$$

Reconstruction of W Surface

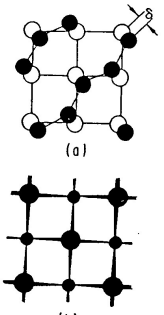
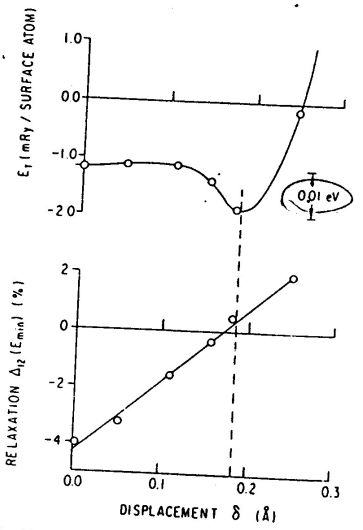


FIG. 1. Atomic displacements for (a) $\bar{M}_5$ phonon with displacements in the ⟨110⟩ direction (open circles indicate bulklike positions); (b) $\bar{M}_1$ phonon with alternating vertical displacements perpendicular to the surface.



(C.L. Fu et al., PRL54)

5. Car-Parrinello Method

Lagrangian Formulation and Ionic Forces

$$\mathcal{L} = \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E_{tot}(\{\phi_i, \mathbf{R}_I\})$$

subject to a set of constraints

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Equations of motion:

$$\mu \ddot{\phi}_i = -\frac{\delta E_{tot}}{\delta \phi_i^*} + \sum_j \Lambda_{ij} \phi_j$$

$$\mathbf{F}_I = M_I \ddot{\mathbf{R}}_I = -\frac{\partial E_{tot}}{\partial \mathbf{R}_I}$$

6. Excitation Properties

- Janak's theorem: meaning of $\epsilon_{n\mathbf{k}\sigma}$

  (corresponding to the Koopman's theorem in HF)

$$\frac{\partial E}{\partial n_{i\sigma}} = \epsilon_{i\sigma}$$

- Ionization Energy vs. Electron Affinity:

  Excitation energy: $\Delta E = A - I$ for $S + S \rightarrow S^+ + S^-$

$$I = E(N) - E(N-1)$$

$$A = E(N+1) - E(N)$$

$$\Delta E = E(N+1) + E(N-1) - 2E(N)$$

7. Spin Density Functional Theory

In the presence of $\mathbf{B}(\mathbf{r})$, the basic variables become

$$\{n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})\}$$

$$n(\mathbf{r}) = \langle\Psi_o|\left(\hat{n}_\uparrow(\mathbf{r}) + \hat{n}_\downarrow(\mathbf{r})\right)|\Psi_o\rangle$$

$$\mathbf{m}_z(\mathbf{r}) = \langle\Psi_o|\left(\hat{n}_\uparrow(\mathbf{r}) - \hat{n}_\downarrow(\mathbf{r})\right)|\Psi_o\rangle$$

Spin Density Functional $E_v[n_\uparrow, n_\downarrow]$**:**

$$\begin{aligned} E_v[n_\uparrow, n_\downarrow] &= \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \mathbf{b}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r})d\mathbf{r} \\ &\quad + T_s[n_\uparrow, n_\downarrow] + E_H[n] + E_{xc}[n_\uparrow, n_\downarrow] \end{aligned}$$

Local Spin-Density Approximation

LSD Exchange Energy Functional:

$$
\begin{aligned}
E_x^{LSD}[n_\uparrow, n_\downarrow] &= 2^{1/3} C_x \int \left[(n_\uparrow)^{4/3} + (n_\downarrow)^{4/3} \right] d\mathbf{r} \\
&= \frac{1}{2} C_x \int n^{4/3} \left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} \right] d\mathbf{r} \\
&= \int n \varepsilon_x(n, \zeta) d\mathbf{r}
\end{aligned}
$$

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}$$

$$\varepsilon_x(n, \zeta) = \varepsilon_x^o(n) + [\varepsilon_x^1(n) - \varepsilon_x^o(n)] f(\zeta)$$

$$f(\zeta) = \frac{1}{2}(2^{1/3} - 1)^{-1} [(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]$$

Self-Interaction Correction

For $N = 1$ system with $n = n_\sigma(\mathbf{r})$ with $\sigma =\uparrow$ or $\downarrow$, the Coulomb and exchange energy must cancel each other:

$$E_H[n_\uparrow] + E_x[n_\uparrow, 0] = 0$$

$$E_c[n_\uparrow, 0] = 0$$

To eliminate self-interaction in an approximate $\bar{E}_{xc}$,

$$E_{xc}^{SIC}[n_\uparrow, n_\downarrow] = \bar{E}_{xc}[n_\uparrow, n_\downarrow] - \sum_{i\sigma} \left(E_H[n_{i\sigma}] + E_x[n_{i\sigma}, 0]\right)$$

8. Electronic Structure Calculation Methods

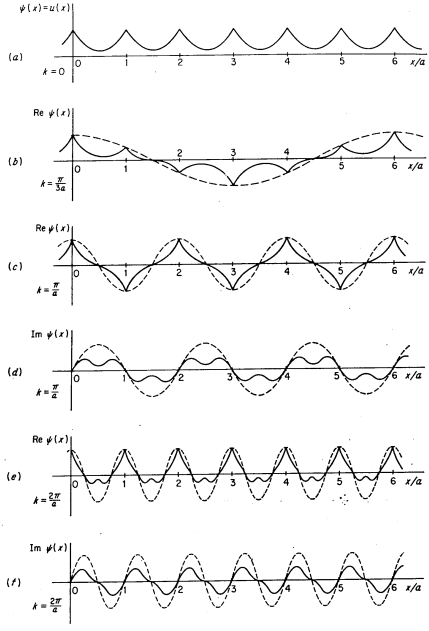
- Tight Binding Basis: (Localized basis functions)
  - Atomic-like orbitals
  - General functions — Gaussians
  - Wannier functions
- Plane wave basis:
  unbiased basis function with a single cutoff parameter

$$\psi_n(\mathbf{r}) = \sum_{\mathbf{G}} c_n(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

- Augmented-plane-wave basis:

$$\phi_{\mathbf{G}} = \begin{cases} \exp i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r} \\ \sum_{\tau lm} u_{\tau l}(r_\tau) Y_{lm}(\Omega_\tau) \end{cases}$$

Phase Change of the Tight-binding wavefunctions



Electronic Structure of Transition Metal Oxides

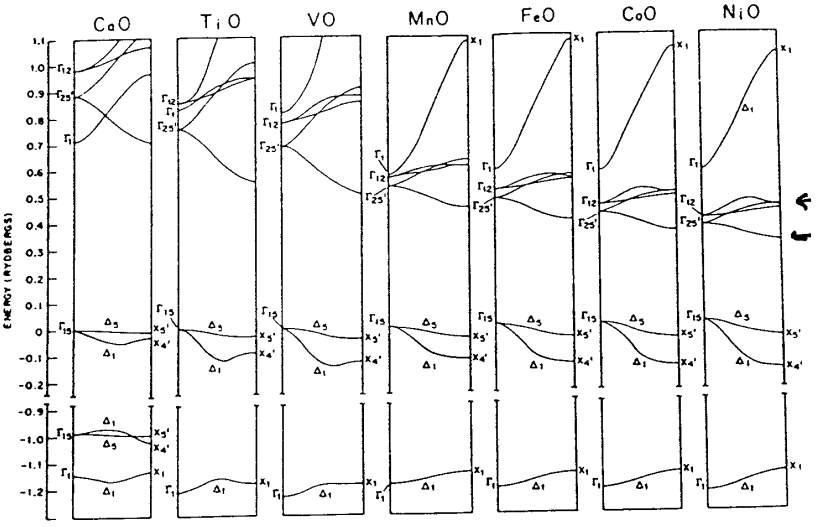
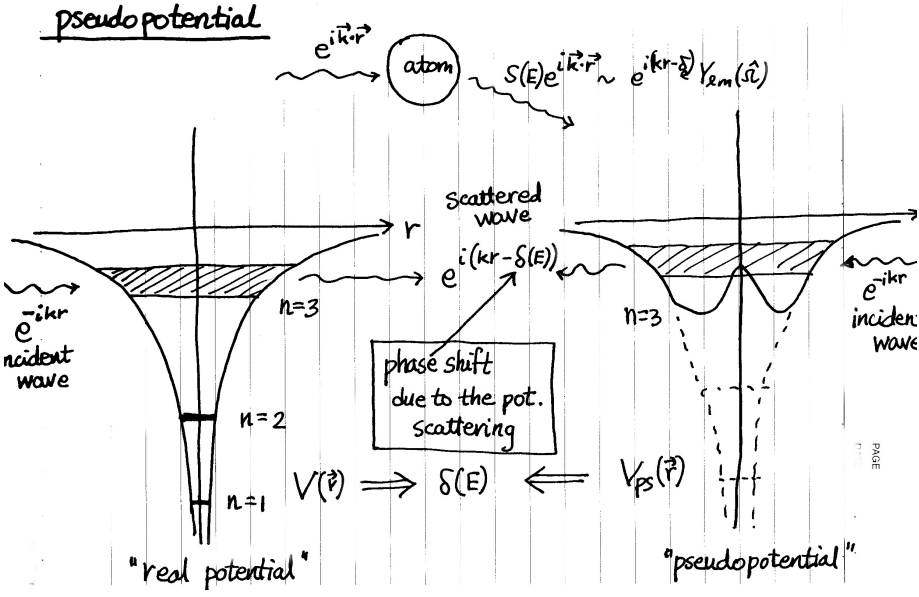


FIG. 2. APW energy-band results for the 3*d* transition-metal oxides plotted along the Δ direction of the Brillouin zone.

(L.F. Mattheiss, PRB5)

Full-potential vs. Pseudo-potential



Logarithmic energy derivatives of radial functions

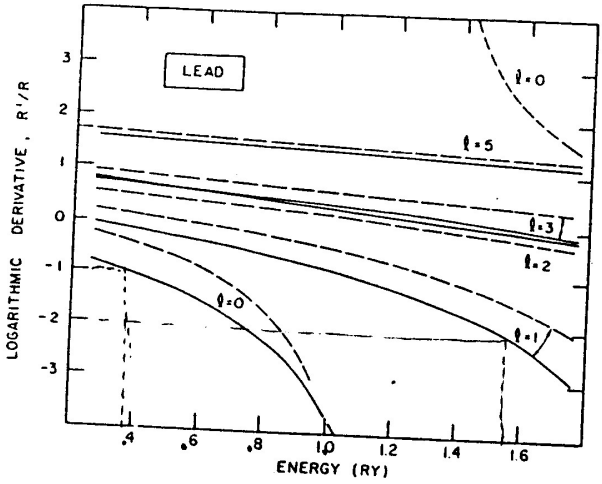
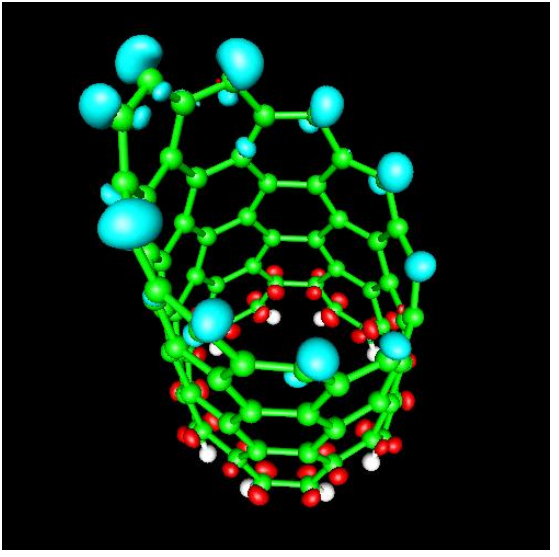


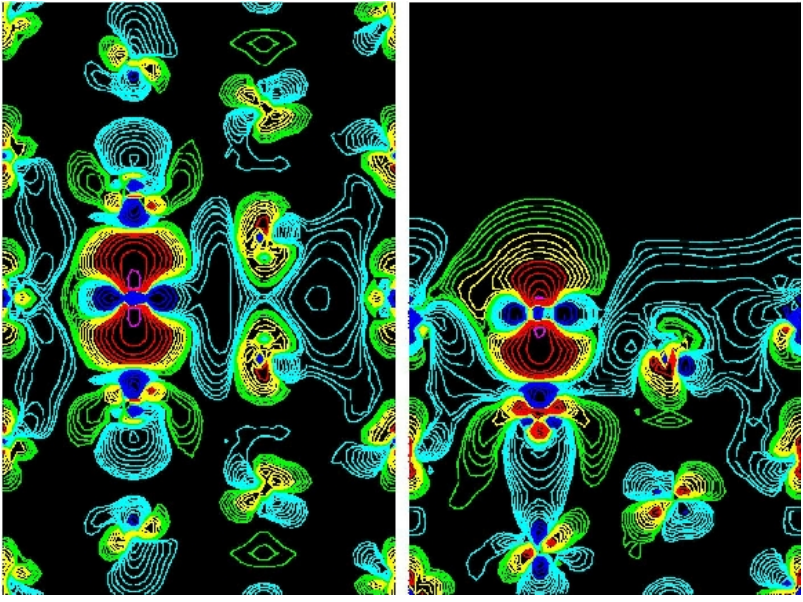
Figure 3-10. Logarithmic derivatives as a function of energy. Solid lines are for lead, and the dashed lines are for zero potential.

9. Examples

Tip of a Carbon Nanotube under External Electric Field: plane wave calculations (J. Ihm et al.)

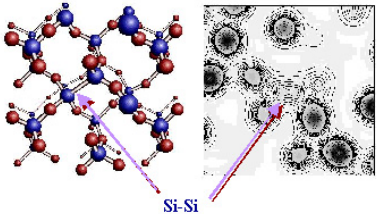


Change of Electron Density due to the Carbon Impurity in the Fe Interface and Surface: FLAPW calculation (S.C. Hong et al.)



Various Oxygen Vacancy Structure inside SiO_2: calculated by the real-space multi-grid method. (K.J. Chang et al.)

Dimer configuration



Puckered configuration