CMS II-2: Density Functional Theory (DFT) and local-density approximation (LDA)

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Outline

- Density Functional Theory (DFT)
- local-density approximation (LDA)
- Exchange-correlation energy functional
- Limitations of LDA
- Attempts on improving LDA

Density Functional Theory (DFT)

Hohenberg-Kohn Theorem, PR136(1964)B864

- The ground-state energy of a system of identical fermions is a unique functional of the particle density.
- This functional attains its minimum value with respect to variation of the particle density subject to the normalization condition when the density has its correct values.

Hohenberg and Kohn

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} V_{ext}(\vec{r}) + \frac{1}{2}\sum_{i=1}^{N} \sum_{j=1(j\neq i)}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Suppose we know $V_{ext}(\vec{r})$, we can find $\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2 \cdots, \vec{r}_N, s_N)$

$$n(\vec{r}_1) = \int dr_2^3 \int dr_2^3 \cdots \int dr_N^3 \left|\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2 \cdots, \vec{r}_N, s_N)\right|^2$$

Theorem : The ground state properties of a many electron system are uniquely determined by its electron distribution ***n(r)***.

➔ All ground state properties of the many electron system are functional of ***n(r).***

$E_T[n], \quad T[n], \quad \cdots$

Hohenberg and Kohn, Phys. Rev. B 136, 864, 1964

Proof :

Suppose there are two $V_{ext}(\vec{r})$ ($\boldsymbol{V_1}$ and $\boldsymbol{V_2}$) have the same ***n(r)***.

Suppose $V_1 \neq V_2 + \text{constant}$

$$\Psi_1 \neq \Psi_2 \qquad (H_1\Psi_1 = E_1\Psi_1 \quad ; H_2\Psi_2 = E_2\Psi_2)$$

Suppose the ground state is nondegenerate, then

$$\langle \Psi_1 | H_1 | \Psi_1 \rangle < \langle \Psi_2 | H_1 | \Psi_2 \rangle \qquad ; \quad H_1 = H_2 + V_1 - V_2$$

$$E_1 < \langle \Psi_2 | H_2 | \Psi_2 \rangle + \langle \Psi_2 | V_1 - V_2 | \Psi_2 \rangle = E_2 + \int d^3r (V_1 - V_2) n(r)$$

$$\int dr_1^3 \cdots \int dr_N^3 \left(V_1(\vec{r}_1) - V_2(\vec{r}_1)\right) \left|\Psi(\vec{r}_1, s_1 \cdots, \vec{r}_N, s_N)\right|^2 = \int dr_1^3 \left(V_1(\vec{r}_1) - V_2(\vec{r}_1)\right) n(\vec{r}_1)$$

$$E_2 < \langle \Psi_1 | H_1 | \Psi_1 \rangle + \langle \Psi_1 | V_2 - V_1 | \Psi_1 \rangle = E_1 + \int d^3r (V_2 - V_1) n(r)$$

$$E_1 - E_2 < \int d^3r (V_1 - V_2) n(r) < E_1 - E_2$$

contratiction

$n_1(\vec{r}) = n_2(\vec{r})$ ⇨ $V_1 = V_2 + \text{constant}$

Total energy functional

P.5

$$E_T[n] = \int V_{ext}(\vec{r})n(\vec{r})d^3r + \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r d^3r' + T[n] + E_{xc}[n]$$

Coulomb energy

Exchange-correlation energy

Minimize E_T subject to the condition $N = \int n(\vec{r})d^3r \Rightarrow n(\vec{r})$

$$\Rightarrow \frac{\delta T[n]}{\delta n} + V_{ext}(\vec{r}) + \int \frac{n(\vec{r})}{|\vec{r}-\vec{r}'|}d^3r + V_{xc}(\vec{r}) = \mu \quad ; \quad V_{xc}[\vec{r}] = \frac{\delta E_{xc}[n]}{\delta n}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i^{occ} |\psi_i(\vec{r})|^2$$

Kohn-Sham eq., PRB(1965)

$\rho_{in} \Rightarrow V_{eff}(r) \Rightarrow \varepsilon_i;\psi_i \Rightarrow \rho_{out}$

$$\rho_{in}^{n+1} = (1-\alpha)\rho_{in}^n + \alpha\rho_{out}^n$$

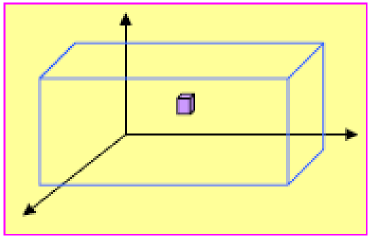
$(\rho(r) = n(r))$

self-consistent scheme

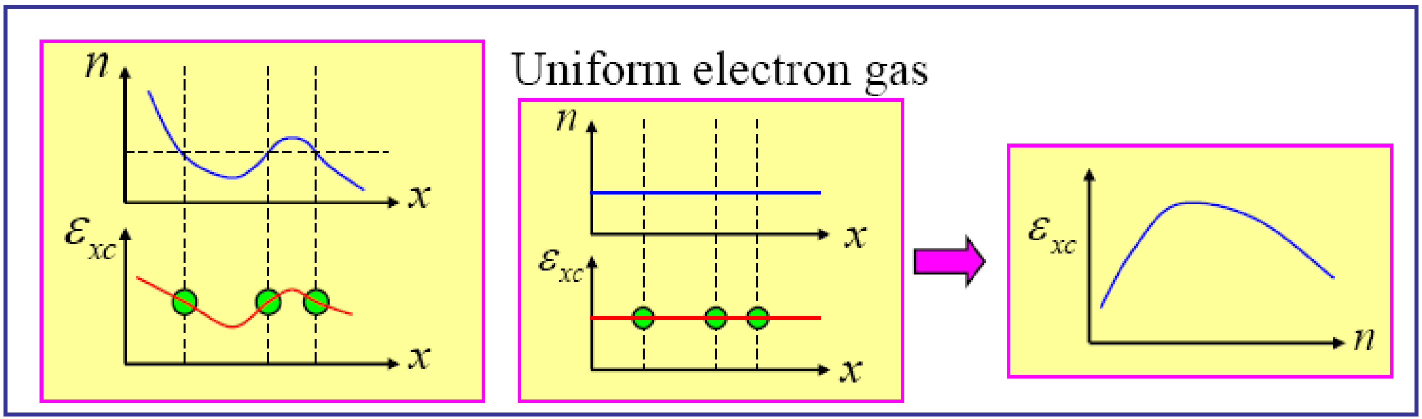
1-2. Local Density Functional Approximation (LDA)

$$E_{xc}[n] = \int \varepsilon_{xc}[n] n(\vec{r}) d^3 r \qquad ; \varepsilon_{xc}[n]$$ exchange-correlation energy per electron

$$\varepsilon_{xc}[n] = \varepsilon_{xc}(n(\vec{r}))$$ **LDA approximation**



$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n} = \frac{d}{dn}\{n \varepsilon_{xc}(n)\}$$



W. Kohn and L. J. Sham, Phys. Rev. B 140, A1133 (1965)

Hartree – Fork approx. $\varepsilon_x = -\frac{0.458}{r_s}$ *where* $n = \left(\frac{4}{3}\pi r_s^3\right)^{-1}$

Quantum Monte Carlo tech. (Ceperly) $\varepsilon_c = \frac{r_s}{1+\beta_1\sqrt{r_s}+\beta_2 r_s}$

$$V_{xc}(r) = \frac{d}{dn}\{n\varepsilon_{xc}(n)\}$$

Local spin-density approximation (LSDA)

$$E_{xc}\left[n_\uparrow, n_\downarrow\right] = \int n(\vec{r})\varepsilon_{xc}(n_\uparrow(\vec{r}), n_\downarrow(\vec{r}))d^3r\,; \quad V_{xc,\sigma}(\vec{r}) = \frac{\delta E_{xc}\left[n_\uparrow(\vec{r}), n_\downarrow(\vec{r})\right]}{\delta n_\sigma(\vec{r})}$$

Generalized gradient approximation (GGA)

$$\varepsilon_{xc}\left[n, \vec{\nabla}n\right] = \varepsilon_{xc}(n(\vec{r}), \vec{\nabla}n(\vec{r}))$$

Exchange-correlation functional

$E^{xc}[n]$ accounts for the difference between the exact ground-state energy and the energy calculated in a Hartree approximation and using the non-interacting kinetic energy $T_0[n]$,

$$E^{xc}[n] \equiv T[n] - T_0[n] + U^{xc}[n]$$

$T[n]$, $T_0[n]\dots$ exact and non-interacting kinetic energy functional
$U^{xc}[n]\dots$ interaction of the electrons with their own exchange-correlation hole n_{xc} defined as (ρ_2 is the two-particle density matrix)

$$\rho_2(\vec{r}, s; \vec{r}', s') \equiv n_s(\vec{r})(n_{s'}(\vec{r}') + n_{xc}(\vec{r}, s; \vec{r}', s'))$$

Spin-polarized LDA (LSDA)

$$E^{xc}[n(\vec{r})] = \int n(\vec{r})\varepsilon_{xc}[n(\vec{r})]d^3r,$$

Exchange-functional (for spin-polarized systems,

$n(\vec{r},\uparrow) \neq n(\vec{r},\downarrow),\ n = n_\uparrow + n_\downarrow$)

$$\begin{aligned}\varepsilon_x[n(\vec{r},\uparrow),n(\vec{r},\downarrow)] &= -\tfrac{3e^2}{4\pi}(3\pi^2)^{1/3}\left\{\tfrac{n(\vec{r},\uparrow)^{4/3}+n(\vec{r},\downarrow)^{4/3}}{n(\vec{r})}\right\} \\ &= \varepsilon_x^p + (\varepsilon_x^f - \varepsilon_x^p)\tfrac{(n_\uparrow/n)^{4/3}+(n_\downarrow/n)^{4/3}-(1/2)^{1/3}}{1-(1/2)^{1/3}}\end{aligned}$$

with $\varepsilon_x^p = \varepsilon_x(n_\uparrow = n_\downarrow = n/2)$ for the paramagnetic (non-spinpolarized) and $\varepsilon_x^f = \varepsilon_x(n_\uparrow = n, n_\downarrow = 0)$ for the ferromagnetic (completely spin-polarized) limits of the functional.

Correlation functional $\varepsilon_c[n(\vec{r},\uparrow),n(\vec{r},\downarrow)]$ fitted to the ground-state energy of a homogeneous electron gas calculated using quantum Monte Carlo simulations and similar spin-interpolations.

Generalized Gradient Approximation (GGA)

General *semi*local approximation to the exchange-correlation energy as a functional of the density and its gradient to fullfill a maximum number of exact relations,

$$E_{xc}^{GGA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\; f(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r})),$$

Exchange correlation potential:

$$V_{xc}[n(\mathbf{r})] = \frac{\partial E_{xc}[n]}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial E_{xc}[n]}{\partial(\nabla n(\mathbf{r}))}.$$

The gradient of the density is usually determined *numerically*.

GGA-PW91

Exchange energy:

$$E_{\mathrm{x}}^{\mathrm{PW91}}[n] = -\int d\mathbf{r}n\frac{3k_F}{4\pi}\ \frac{1+0.1965s\sinh^{-1}(7.796s)+(0.274-0.151e^{-100s^2})s^2}{1+0.1964s\sinh^{-1}(7.796s)+0.004s^4}$$

Correlation energy:

$$E_{\mathrm{c}}^{\mathrm{PW91}}[n] = \int d\mathbf{r}n\left(\varepsilon_{\mathrm{c}}(\mathbf{r}_s,\zeta)+H(t,r_s,\zeta)\right)$$

with $k_F = (3\pi^2 n)^{1/3}$, $s = |\nabla n|/2k_F n$, $t = |\nabla n|/2gk_s n$, $g = [(1+\zeta)^{2/3}+(1-\zeta)^{2/3}]/2$, and $k_s = (4k_F/\pi)^{1/2}$.

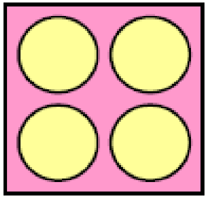
1-3 First-principles Calculation Method

(i) Plane Wave : (Pseudopotential Method)

$$u_k(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_n C_n^{(\vec{k})} e^{i\vec{G}_n \cdot \vec{r}}$$

Use pseudopotential to replace the effect of the core electron

(ii) Muffin-Tin Method : LAPW, LMTO, FPLAPW , FPLMTO

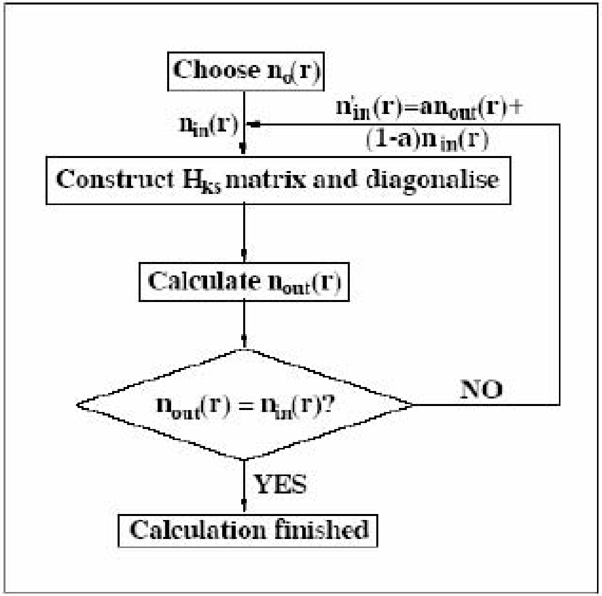


$$\chi_n(\vec{r}) = \begin{cases} e^{i\vec{G}_n \cdot \vec{r}} \\ \sum_{n\ell m} A_{n\ell m} R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \end{cases}$$

(iii) Atomic Orbital : LCAO, Tight Binding Method

$$\psi_{\vec{k}}(\vec{r}) = \sum_{n\ell m} C_{n\ell m}^{(\vec{k})} \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{r}+\vec{R})} \phi_{n\ell m}(\vec{r} - \vec{R})$$

Self-consistent field (SCF) calculations



- $V_H(\mathbf{r})$ and $V_{XC}(\mathbf{r})$ depend on $n(\mathbf{r})$
- $n(\mathbf{r})$ depends on $\{\psi_i(\mathbf{r})\}$
- But we are trying to find $\{\psi_i(\mathbf{r})\}$ and the corresponding energy levels — we need *self-consistency*

Insufficiencies of LDA

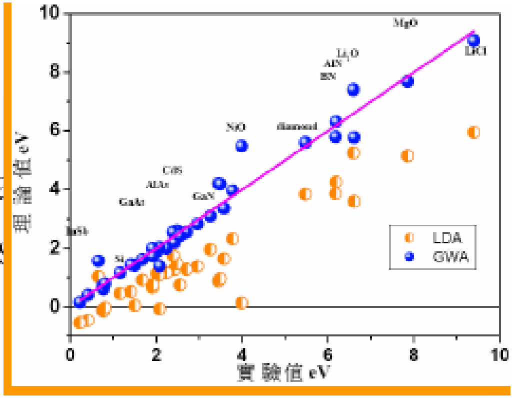
- Poor eigenvalues, PRB23, 5048 (1981)
- Lack of derivative discontinuity at integer N, PRL49, 1691 (1982)
- Gaps too small or no gap, PRB44, 943 (1991)
- Spin and orbital moment too small, PRB44, 943 (1991)
- Especially for transition metal oxides

- **Band-gap problem**:

- HKS theorem not valid for excited states ⟶ ba

semiconductors and insulators are always underes

- Possible solutions: - Hybrid-functionals lead to



- LDA+U, GW, SIC increase correlation gaps

- **Overbinding**:

- LSDA: too small lattice constants, too large cohesive energies, too high bulk moduli

- Possible solutions: - GGA: overbinding largely corrected (tendency too overshoot for the heaviest elements)

- The use of the GGA is mandatory for calculating adsorption energies, but the choice of the "correct" GGA is important.

- Neglect of strong correlations

- Exchange-splitting underestimated for narrow d- and f-bands

- Many transition-metal compounds are Mott-Hubbard or charge-transfer insulators, but DFT predicts metallic state

- Possible solutions: - Use LDA+U, GW, SIC, . . .

- Neglect of van-der Waals interactions

- vdW forces arise from mutual dynamical polarization of the interacting atoms $\longrightarrow$ not included in any DFT functional

- Possible solution: - Approximate expression of dipole-dipole vdW forces on the basis of local polarizabilities derived from DFT ??

Attempts on improving LDA

- Self-interaction correction (SIC) PRL65(1990)1148
- Optimized effective potential method (OEP)
- Hartree-Fock (HF) method, PRB48(1993)5058
- Time-dependent density functional (TDDFT)
- Quantum Monte-Carlo method (QMC)
- Dynamical Mean Field Theory (DMFT)
- GW approximation (GWA), PRB46(1992)13051, PRL74(1995)3221
- LDA+Hubbard U (LDA+U) method, PRB44(1991)943, PRB48(1993)16929

LDA+U PRB44(1991)943, PRB48(1993)169

- Delocalized s and p electrons : LDA
- Localized d or f electrons : +U
  using on-site d-d Coulomb interaction
  (Hubbard-like term)

$$U \sum_{i \neq j} n_i n_j$$

instead of averaged Coulomb energy

$$UN(N-1)/2$$

CMS II-2 Hands-on: xmgrace, equilibrium lattice constant, and LDA vs GGA

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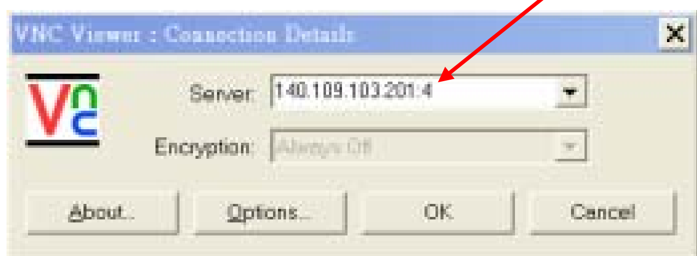
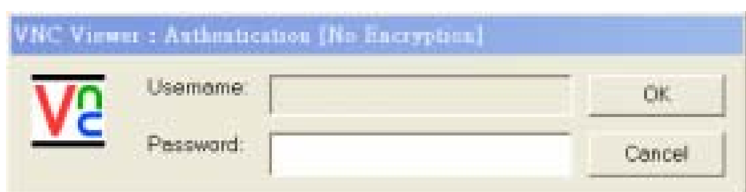
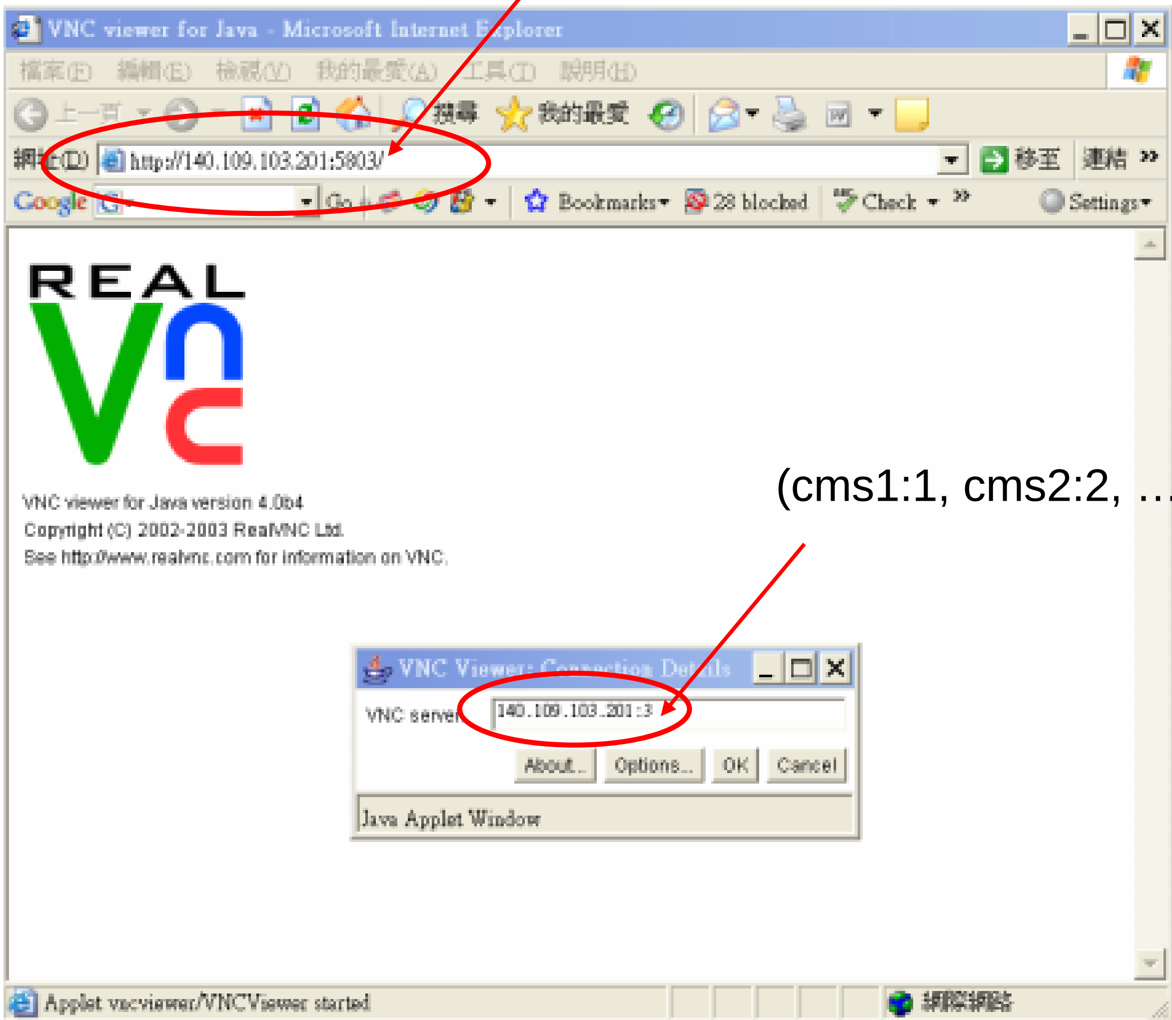
1. login your account, change password of vnc (X-window) server:
%vncpasswd
2. Start vncserver:
%vncserver
………..
Log file is /home/cms1/.vnc/hcserver.cluster:4.log
3. Open vnc viewer on your PC



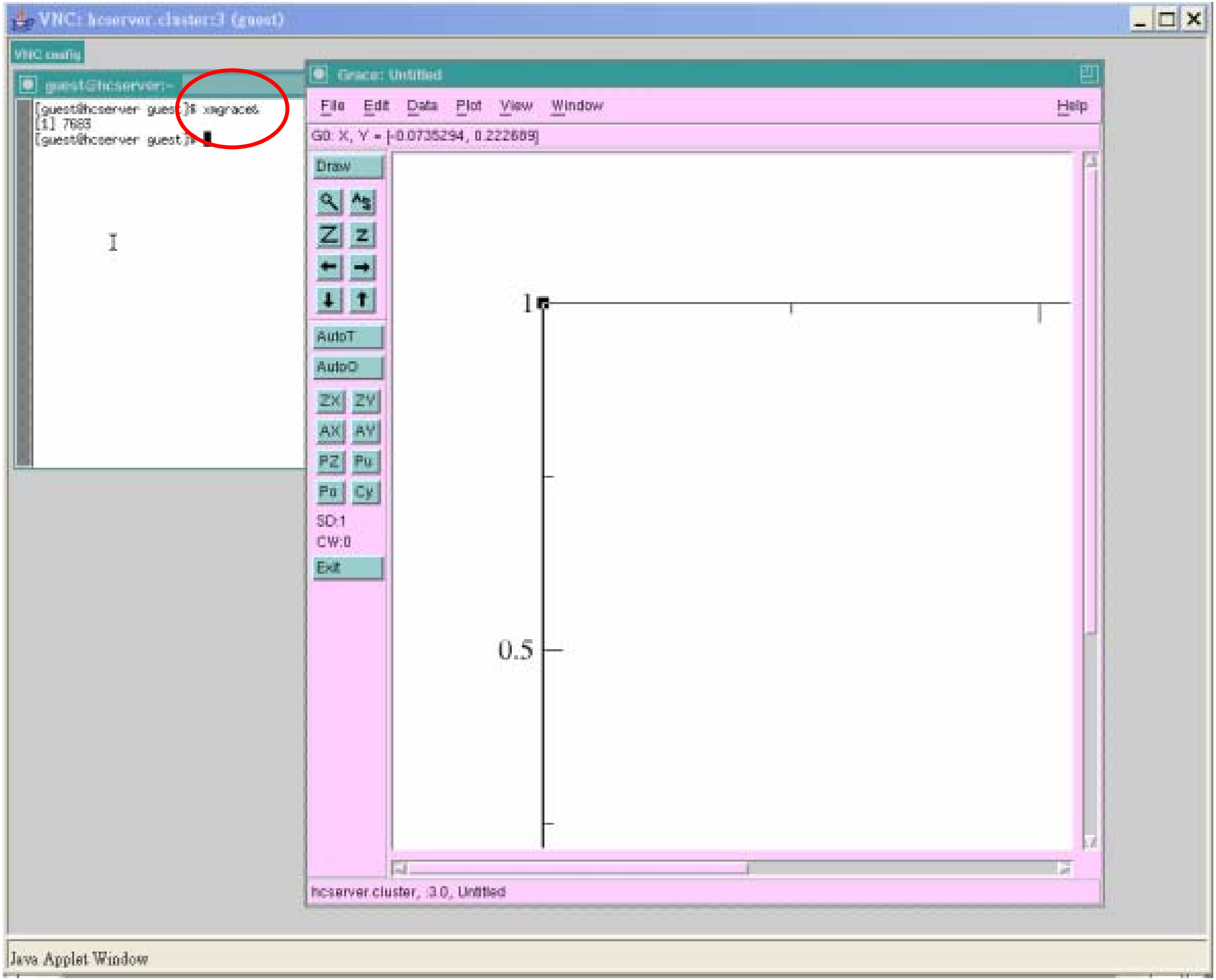
4. key-in your vnc password



(5801, 5802, 5803)



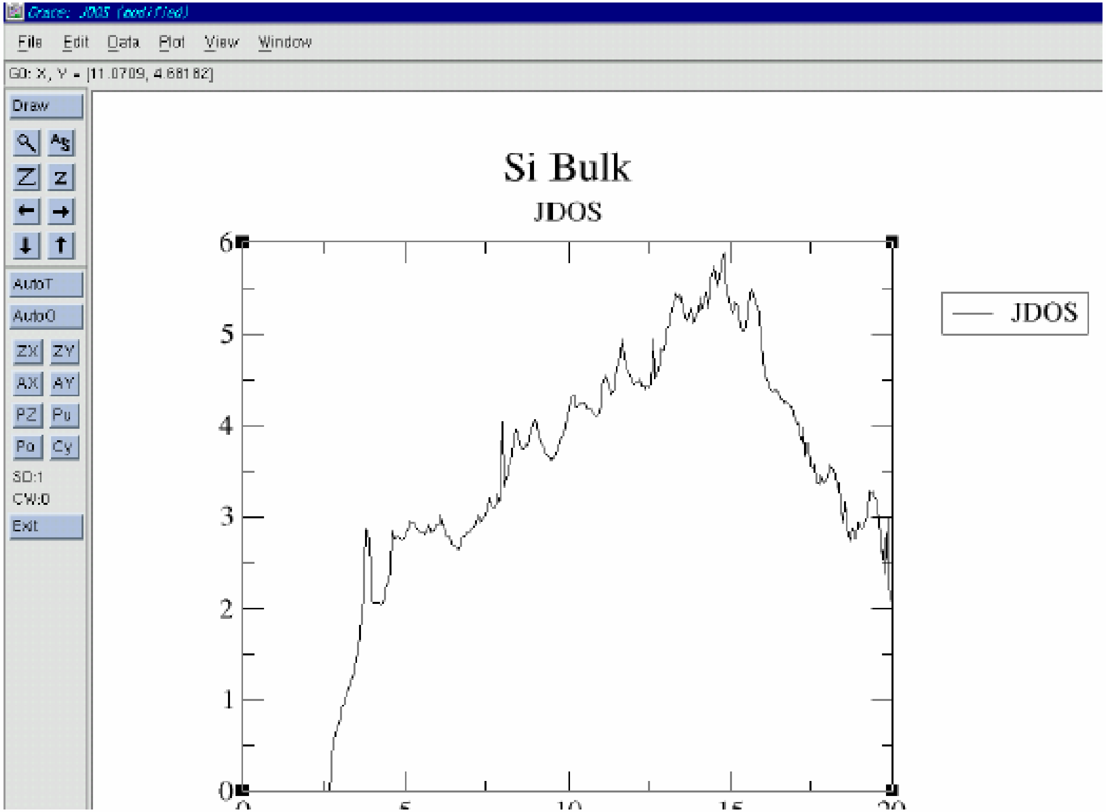
(cms1:1, cms2:2, …)


VNC: hcserver.cluster:3 (guest)
VNC config
guest@hcserver:~
[guest@hcserver guest]$ xmgrace&
[1] 7683
[guest@hcserver guest]$
Grace: Untitled
File
Edit
Data
Plot
View
Window
Help
G0: X, Y = [-0.0735294, 0.222689]
Draw
AutoT
AutoO
ZX
ZY
AX
AY
PZ
Pu
Po
Cy
SD:1
CW:0
Exit
1
0.5
hcserver.cluster, :3.0, Untitled
Java Applet Window

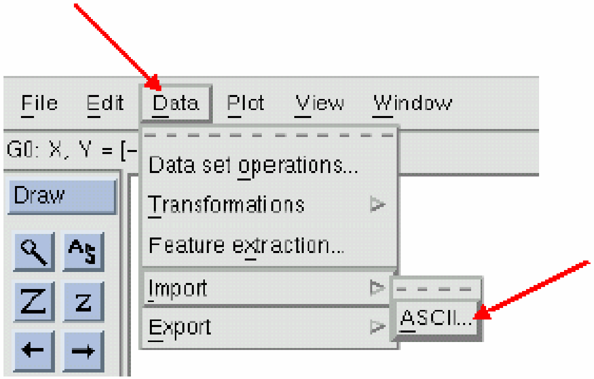
xmgrace

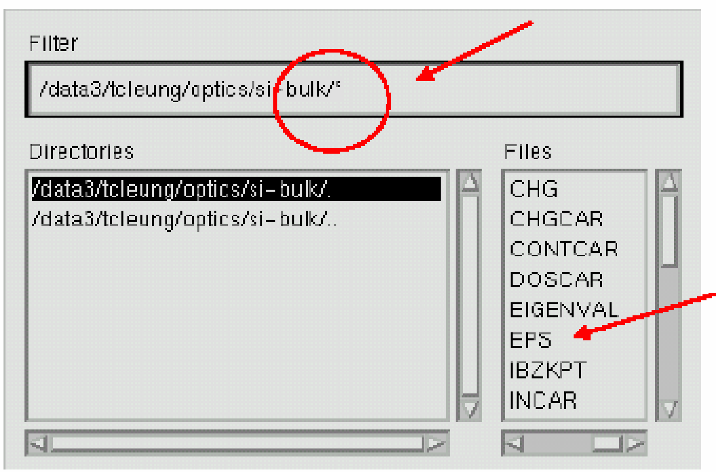
How to use xmgrace to draw lines ?

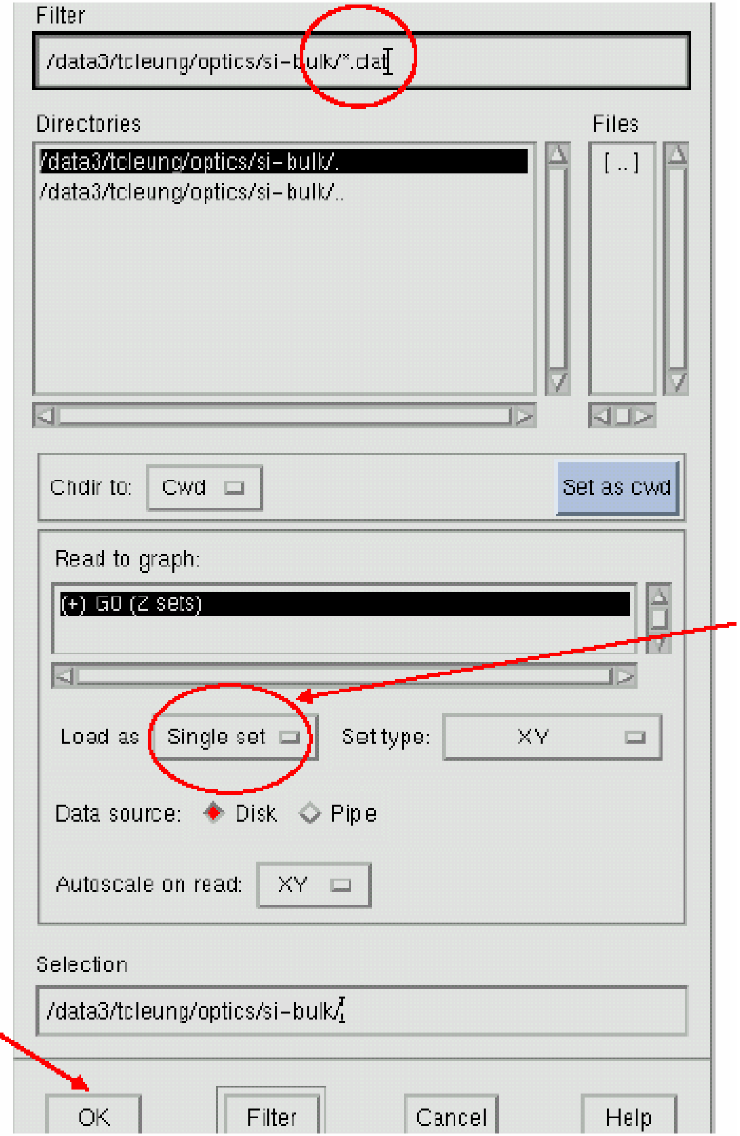
%xmgrace filename (default *.dat)



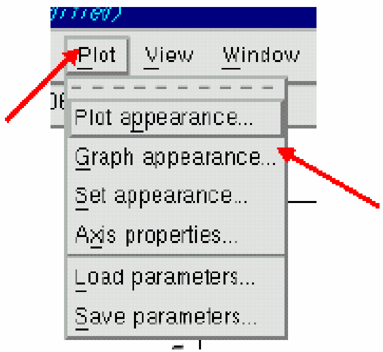
How to import a data file ?

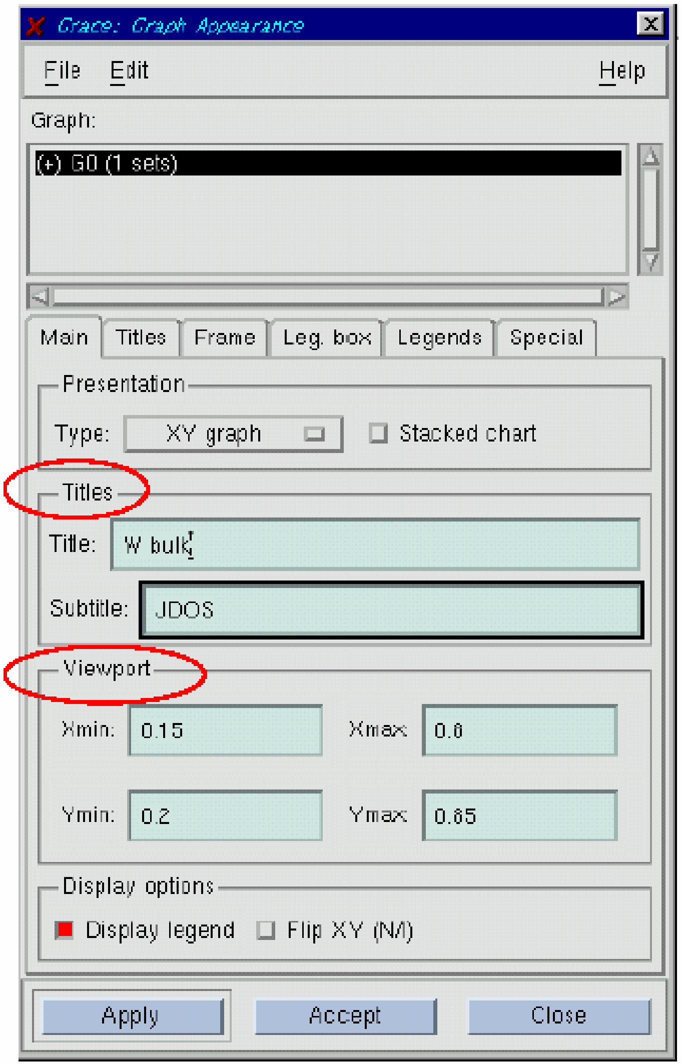




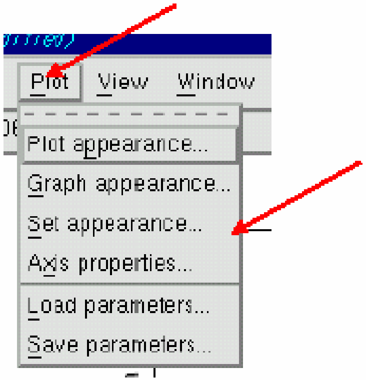


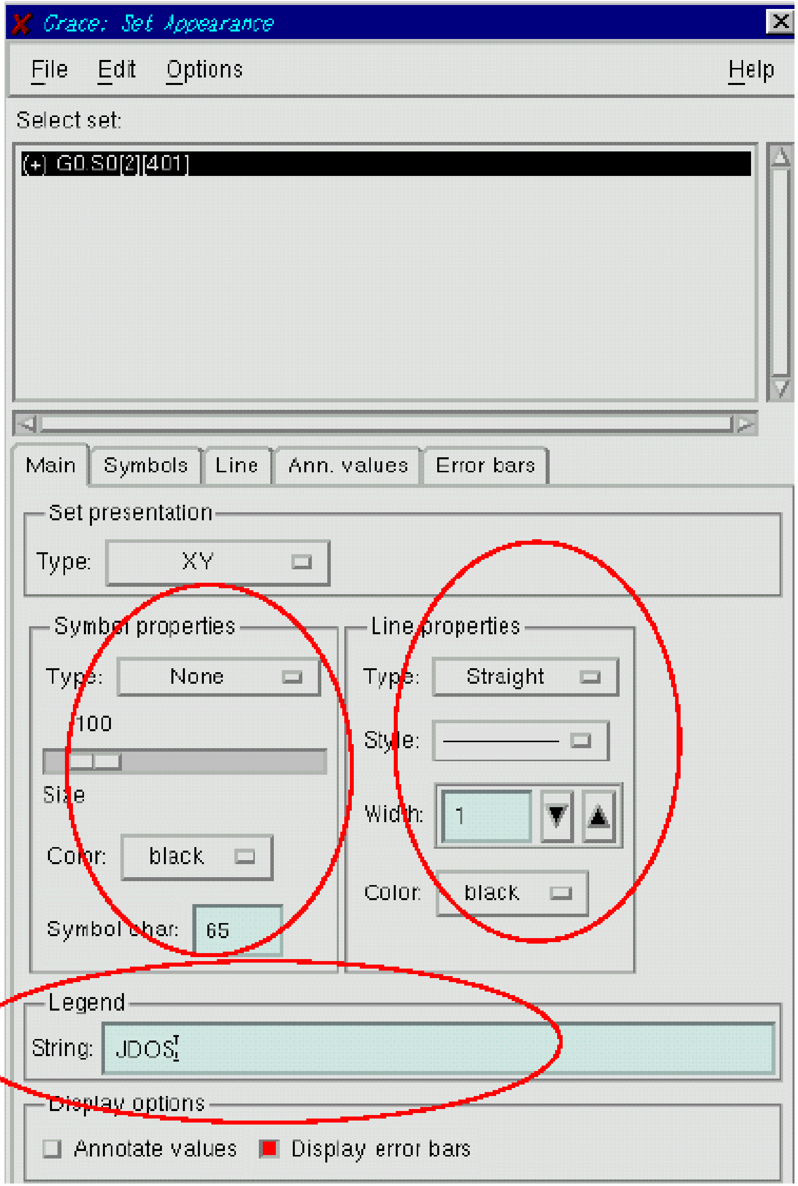
How to set the Titles and the Viewport ?



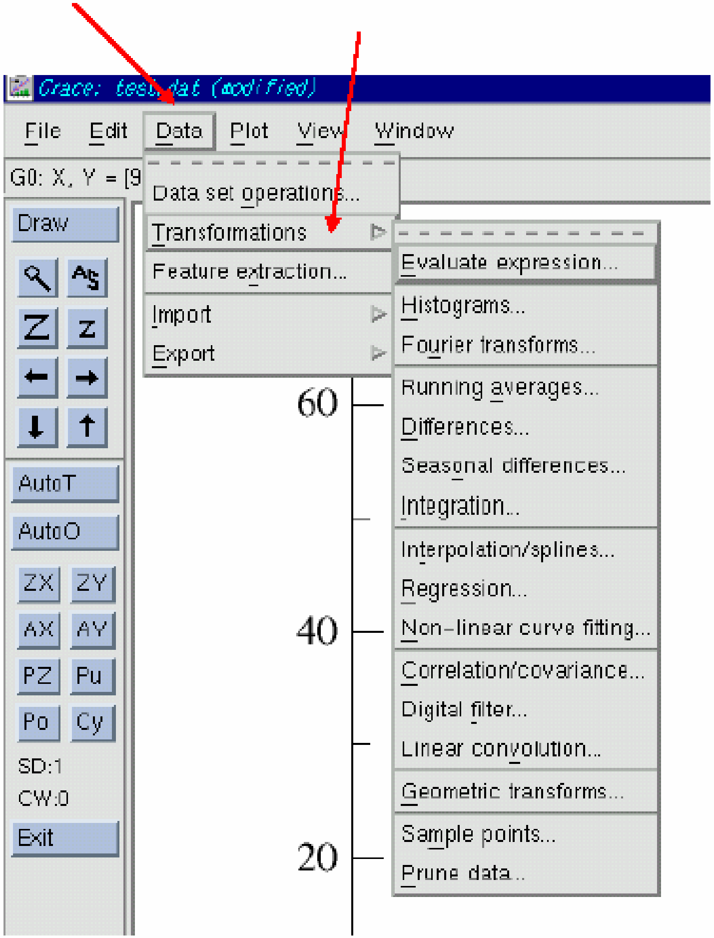


How to set Line properties Symbol properties, Legend ?

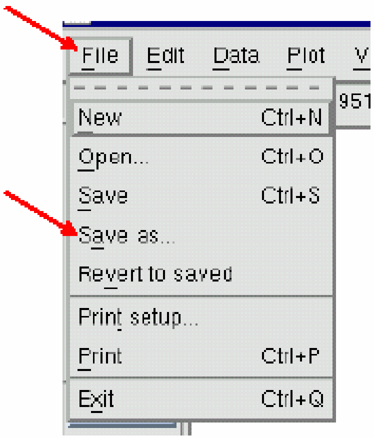


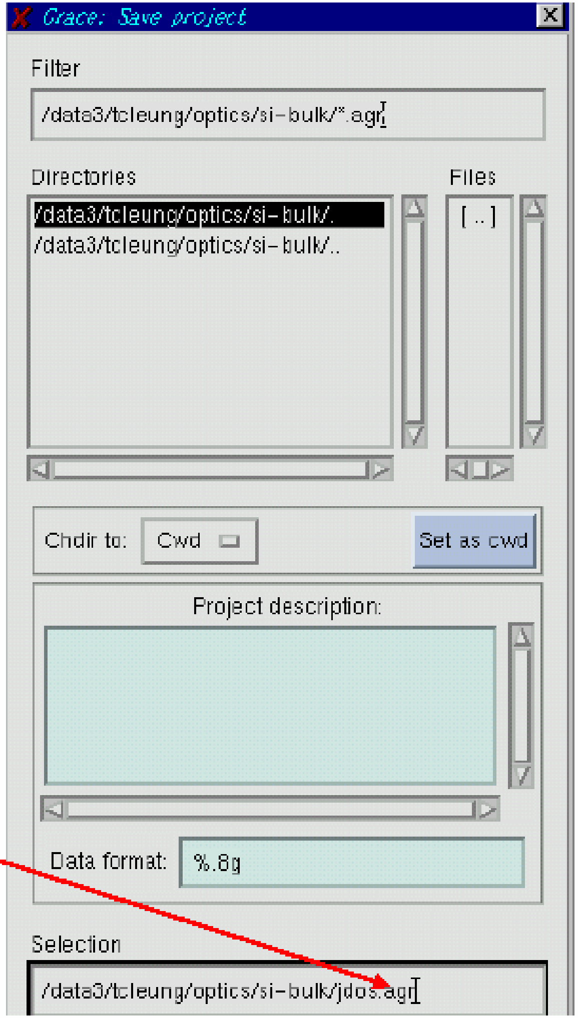


How to analyze the data ?



How to save the result (*.agr) ?

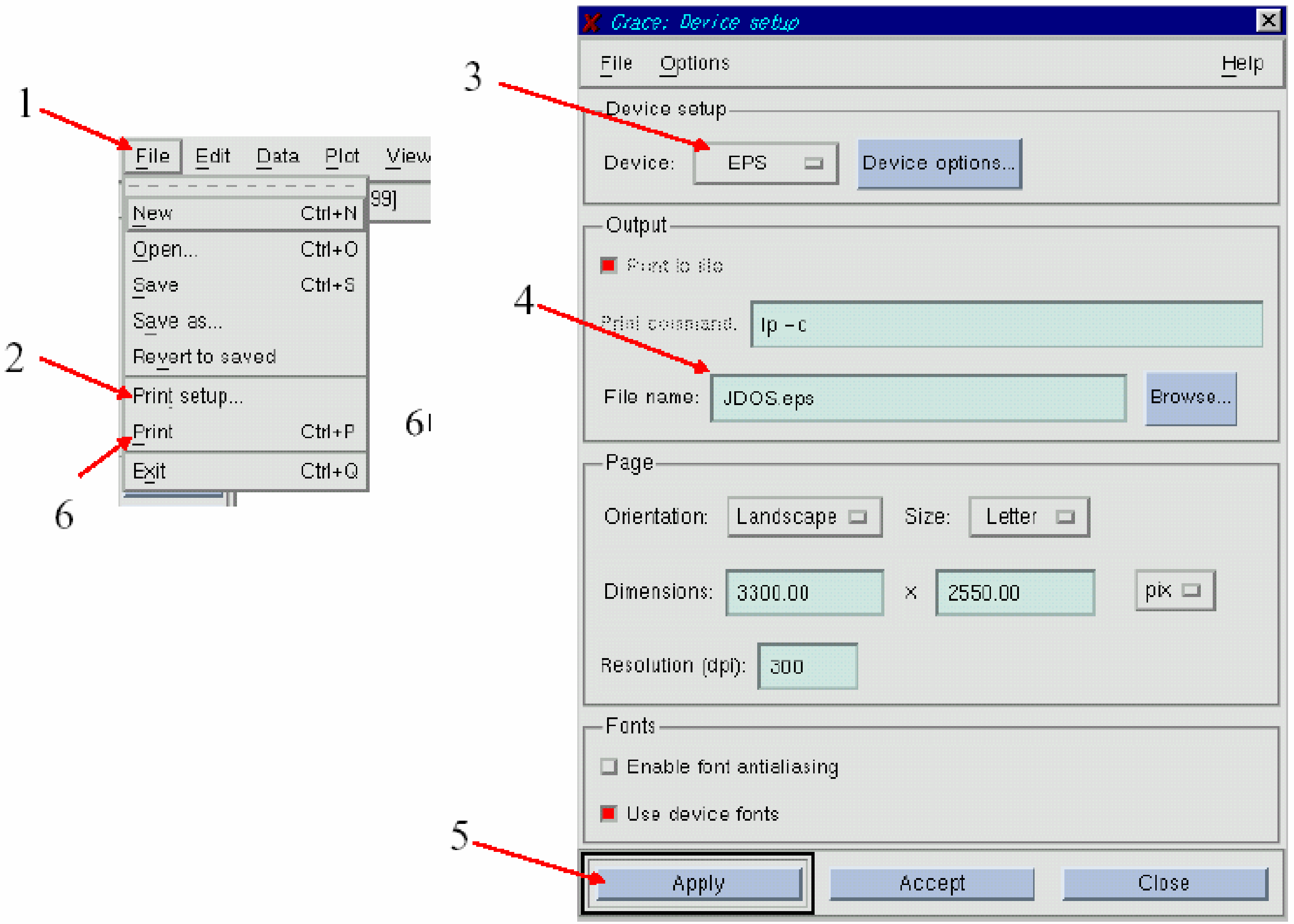




You can use the following statement to redraw the results.

%xmgrace jdos.agr

How to print out the result (*.eps) ?



Optimize lattice constant

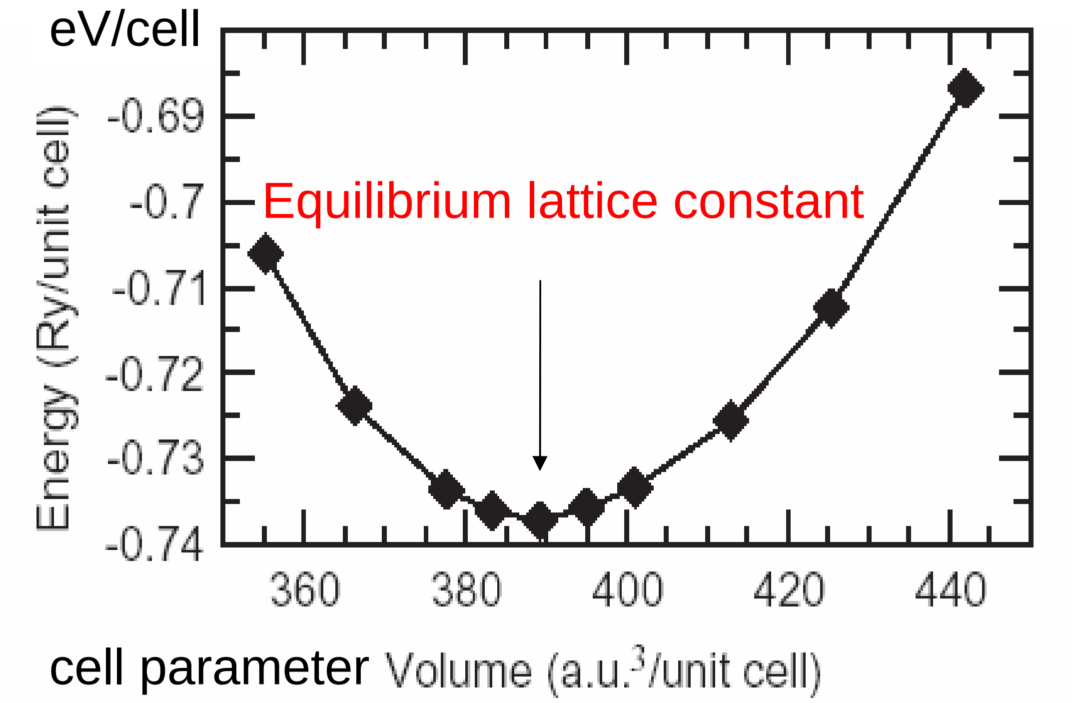


Fig 1. Total energy (lower), total and local Cr spin magnetic moments (upper) of CrO_2 as a function of volume, c/a is fixed at 0.664. The total energy is relative to −4805.0 Ry/unit cell. The experimental unit cell volume is 385 a.u.^{3}.

Work list

- Setup bulk calculation for Si(Dia) using sufficient k-points, and experimental lattice structure as input
- Vary the lattice from –5% to 5% and redo the bulk calculation to find out the equilibrium lattice constant of Si(Dia)
- Setup a convergent bulk calculation for Cu(FCC)
- Find out the equilibrium lattice constant for Cu(FCC) using LDA and GGA

Optimize the Si(Dia) lattice constant

- Revise the lattice constant in POSCAR by 5.43*0.99, redo the bulk calculation to obtain the cohesive energy
- Redo 5.43*0.98…, 5.43*0.95, record the cohesive energies
- Redo 5.43*1.01, …, 5.43*1.05, record the cohesive energies
- Plot the energy (E) vs lattice constant (A) plot for Si(Dia) using xmgrace

LDA vs GGA

- Setup a convergent bulk calculation for Cu(FCC) using LDA
- Find the equilibrium lattice constant for Cu(FCC) using LDA
- Redo the calculations using GGA approximation by using GGA pseudopotential (potpaw_GGA) and adding a new line in INCAR:

  GGA = 91

Homework

please Email to jeng@phys.sinica.edu.tw

- Using sufficient k-points to find out the equilibrium lattice constants of Si(Dia) and C(Dia) and compare with the experimental lattice constants
- Make a cohesive energy (E) vs lattice constant (A) plot for Si(Dia) and C(Dia) using xmgrace
- Make a E-A plot for Cu(FCC) using LDA and GGA