UNIVERSITÀ
DEGLI STUDI
DI PADOVA

Density Functional Theory

Modulo: Funzionale Densità

Chimica Computazionale
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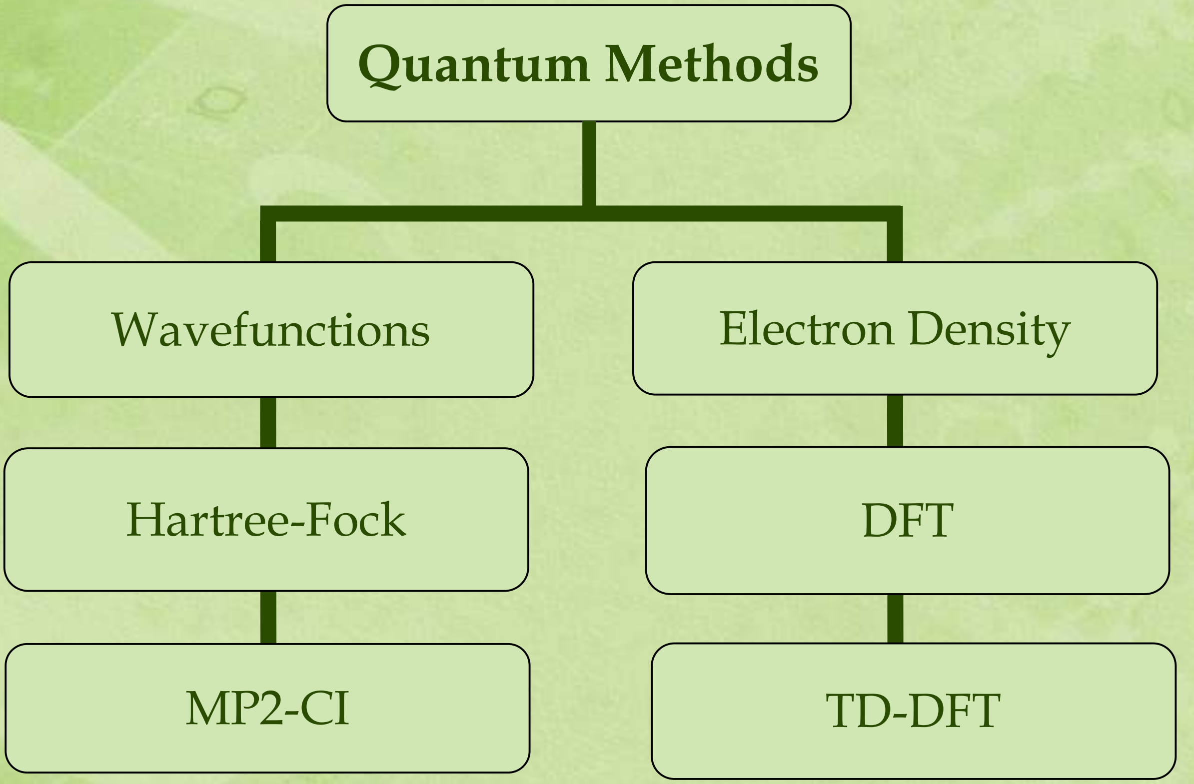
Density functional theory (DFT) has revolutionized the quantun chemistry development of the last 20 years

DFT allows to get information about the energy, the structure and the molecular properties of molecules at lower costs that traditions approaches based on the wavefunction use.



Quantum Methods

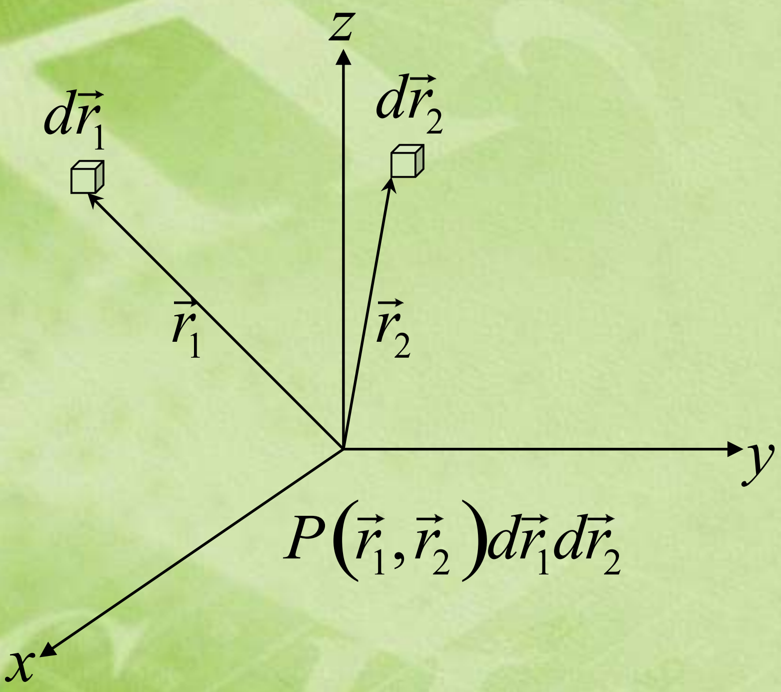
- Wavefunctions
  - Hartree-Fock
    - MP2-CI
- Electron Density
  - DFT
    - TD-DFT

The HF equations have to be solved iteratively because V_{HF} depends upon solutions (the orbitals). In practice, one adopts the LCAO scheme, where the orbitals are expressed in terms of N basis functions, thus obtaining matricial equations depending upon N^4 bielectron integrals.

Correlation energy

Exchange correlation: Electrons with the same spin (m_s) do not move independently as a consequence of the Pauli exclusion principle. $\Psi = 0$ if two electrons with the same spin occupy the same point in space, independently of their charge. HF theory treats exactly the exchange correlation generating a non local exchange correlation potential.

Coulomb correlation: Electrons cannot move independently as a consequence of their Coulomb repulsion even though they are characterized by different spin (m_s). HF theory completely neglects the Coulomb correlation thus generating, in principle, significant mistakes. Post HF treatments are often necessary.



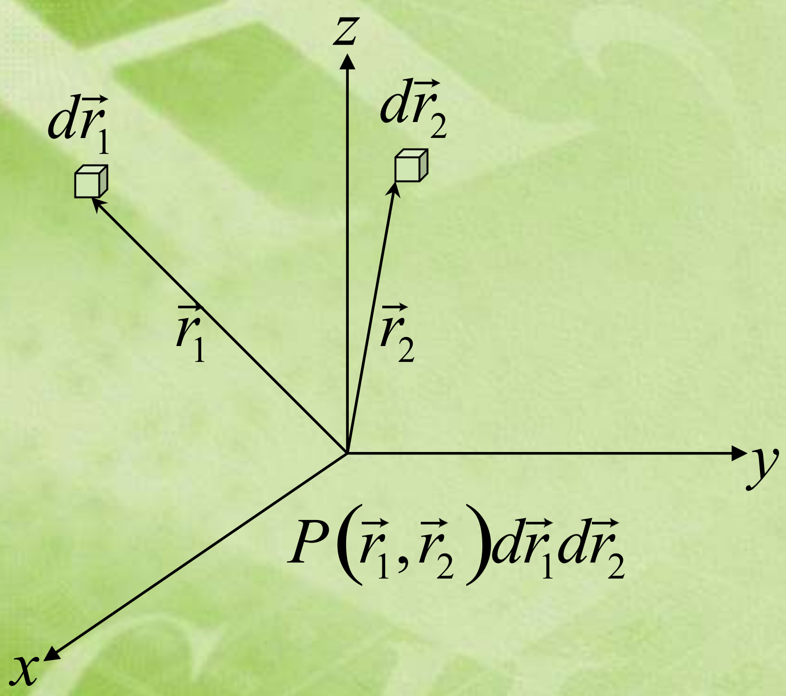
$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle$$

$$\chi_1(\mathbf{x}_1) = \psi_1(\vec{r}_1)\alpha(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\vec{r}_2)\beta(\omega_2)$$

$$\Psi\left(\mathbf{x}_1,\mathbf{x}_2\right)=\left|\chi_1\left(\mathbf{x}_1\right)\chi_2\left(\mathbf{x}_2\right)\right\rangle=\frac{1}{\sqrt{2!}}\begin{vmatrix}\chi_1\left(\mathbf{x}_1\right) & \chi_1\left(\mathbf{x}_2\right)\\ \chi_2\left(\mathbf{x}_1\right) & \chi_2\left(\mathbf{x}_2\right)\end{vmatrix}$$

$$\left|\Psi\right|^2 d\mathbf{x}_1 d\mathbf{x}_2=\frac{1}{2}\left\{\begin{matrix}\psi_1\left(\vec{r}_1\right)\alpha\left(\omega_1\right)\psi_2\left(\vec{r}_2\right)\beta\left(\omega_2\right)- \\ \psi_1\left(\vec{r}_2\right)\alpha\left(\omega_2\right)\psi_2\left(\vec{r}_1\right)\beta\left(\omega_1\right)\end{matrix}\right\}^2 d\mathbf{x}_1 d\mathbf{x}_2$$



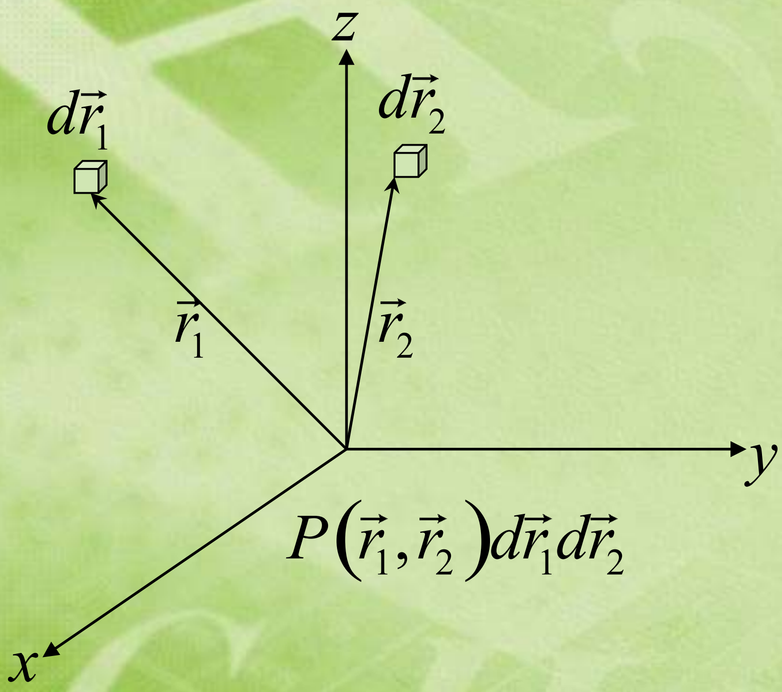
If the electrons have not the same spin

$$P(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2 = \int d\omega_1 d\omega_2 \left|\Psi\right|^2 =$$

$$\tfrac{1}{2}\left[\left|\psi_1(\vec{r}_1)\right|^2\left|\psi_2(\vec{r}_2)\right|^2 + \left|\psi_1(\vec{r}_2)\right|^2\left|\psi_2(\vec{r}_1)\right|^2\right] d\vec{r}_1 d\vec{r}_2$$

if $\psi_1 = \psi_2$

$$P(\vec{r}_1,\vec{r}_2) = \left|\psi_1(\vec{r}_1)\right|^2\left|\psi_1(\vec{r}_2)\right|^2 \qquad P(\vec{r}_1,\vec{r}_1) = \left|\psi_1(\vec{r}_1)\right|^2\left|\psi_1(\vec{r}_1)\right|^2 \neq 0$$



$$P(\vec{r}_1,\vec{r}_2)d\vec{r}_1 d\vec{r}_2$$

If the electrons have the same spin

$$\chi_1(\mathbf{x}_1) = \psi_1(\vec{r}_1)\beta(\omega_1)$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\vec{r}_2)\beta(\omega_2)$$

$$P(\vec{r}_1,\vec{r}_2) = \tfrac{1}{2}\left\{ \begin{array}{l} |\psi_1(\vec{r}_1)|^2 |\psi_2(\vec{r}_2)|^2 + |\psi_1(\vec{r}_2)|^2 |\psi_2(\vec{r}_2)|^2 - \\ \left[\begin{array}{l} \psi_1^*(\vec{r}_1)\psi_2(\vec{r}_1)\psi_2^*(\vec{r}_2)\psi_1(\vec{r}_2) + \\ \psi_1(\vec{r}_1)\psi_2^*(\vec{r}_1)\psi_2(\vec{r}_2)\psi_1^*(\vec{r}_2) \end{array} \right] \end{array} \right\}$$

$$P(\vec{r}_1,\vec{r}_1) = 0$$

Information provided by Ψ is redundant

benzene

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$N = 42e^-$

Number of terms in the determinantal form **Ψ** : $N! = 1.4 \times 10^{51}$

Number of Cartesian dimensions: $3N = 126$

Ψ *is a very complex object including more information than we need!*

The use of electron density allows to limit the redundant information

The electron density is a function of three coordinates no matter of the electron number.

Timetable

- 1920s: **Introduction of the Thomas-Fermi model.**
- 1964: Hohenberg-Kohn paper proving existence of exact DF.
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA. DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello) (Now one of PRL's top 10 cited papers).
- 1988: Becke and LYP functionals. DFT useful for some chemistry.
- 1998: Nobel prize awarded to Walter Kohn in chemistry for development of DFT.

Quotation: "If I have seen further [than certain other men] it is by standing upon the shoulders of giants."*

Isaac Newton (1642–1727), British physicist, mathematician.
Letter to Robert Hooke, February 5, 1675.

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*With reference to his dependency on Galileo's and Kepler's work in physics and astronomy.

(a) Thomas, L. H. *Proc. Cambridge Philos. Soc.* **1927**, *23*, 542;
(b) Fermi, E. *Z. Phys.* **1928**, *48*, 73;
(c) Dirac, P. A. M. *Cambridge Philos. Soc.* **1930**, *26*, 376;
(d) Wigner, E. P. *Phys. Rev.* **1934**, *46*, 1002.

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Thomas, L. H.
1903-1992

Fermi, E.
1901-1954

Dirac, P.M.A.
1902-1984

Wigner, E.
1902-1995

(a) Hartree, D. R. *Proc. Cambridge Phil. Soc.* **1928**, *24*, 89;
(b) ibidem **1928**, *24*, 111;
(c) ibidem **1928**, *24*, 426;
(d) Fock, V. Z. *Physic* **1930**, *61*, 126;
(e) Slater, J. C. *Phys. Rev.* **1930**, *35*, 210.

Hartree, D.R.
1897-1958

Fock, D.R.
1898-1974

Slater J. C.
1900 -1976

Definitions

Function: *a prescription which maps one or more numbers to another number:*

$$y = f(x) = x^2$$

Definitions

Operator: a prescription which maps a function onto another function:

$$\hat{F} = \frac{\partial^2}{\partial x^2}$$

$$\hat{F} f\left(x\right) = \frac{\partial^2 f\left(x\right)}{\partial x^2}$$

Definitions

Functional: A functional takes a function as input and gives a number as output. An example is:

$$F\left[f\left(x\right)\right]=y$$

Here $f(x)$ is a function and y is a number. An example is the functional to integrate x from -∞ to ∞.

$$F[f]=\int_{-\infty}^{\infty} f(x)dx$$

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Vito Volterra
1860 - 1940

In base a un regio decreto emanato il 28 agosto 1931 i docenti delle università italiane avrebbero dovuto giurare di essere fedeli non solo allo statuto albertino e alla monarchia, ma anche al regime fascista.

Francesco ed Edoardo Ruffini e Fabio Luzzatto (giuristi);
Giorgio Levi Della Vida (orientalista);
Gaetano De Sanctis (storico dell'antichità);
Ernesto Buonaiuti (teologo);
Vito Volterra (matematico);
Bartolo Nigrisoli (chirurgo);
Marco Carrara (antropologo);
Lionello Venturi (storico dell'arte);
Giorgio Errera (chimico);
Piero Martinetti (studioso di filosofia).

Nel 1938, con la promulgazione delle Leggi razziali, perdettero il posto i professori considerati di origine ebraica in base alla normativa razziale

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ab-initio methods can be interpreted as a functional of the wavefunction, with the functional form completely known!

$$E[\Psi]=\frac{\int \Psi^*(x_1,\ldots,x_N)\hat{H}\Psi(x_1,\ldots,x_N)dx_1\ldots dx_N}{\int \Psi^*(x_1,\ldots,x_N)\Psi(x_1,\ldots,x_N)dx_1\ldots dx_N}$$

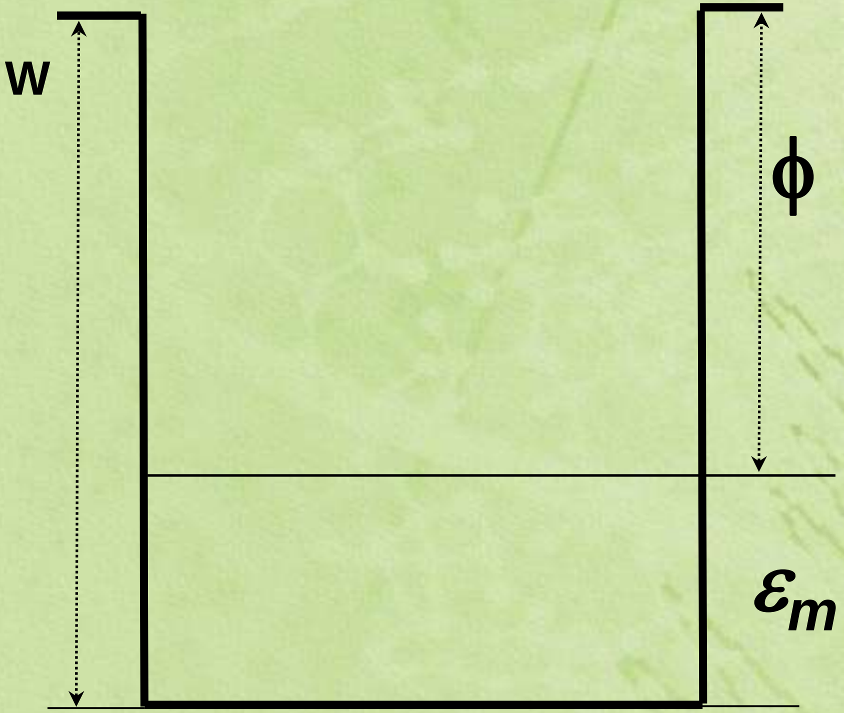
Thomas–Fermi-Dirac Model

Electrons are uniformly distributed over the phase space in cells of $(2\pi h)^3$

Each cell may contain up to two electrons with opposite spins

Electrons experience a potential field generated by the nuclear charge and by the electron distribution itself.

Let us consider a free electron gas



Let us consider a free electron gas

$$\frac{\mathcal{N}_A}{V} = 6.023\times10^{23}\,\frac{atoms}{mol}\times\frac{8.92\,\frac{g}{cm^3}}{63.5\,\frac{g}{mol}} = 8.47\times10^{22}\,\frac{electrons}{cm^3}$$

$$\frac{\mathcal{N}_A}{V} = 6.023\times10^{23}\,\frac{atoms}{mol}\times\frac{Z\rho}{at.weight}$$

$$P = \frac{82.06\left(\frac{cm^3 atm}{mol K}\right)293K}{7.11\left(\frac{cm^3}{mol}\right)} = 3381 atm$$

$$7.11\left(\frac{cm^3}{mol}\right) = \frac{6.023\times10^{23}\,\frac{atoms}{mol}}{8.47\times10^{22}\,\frac{electrons}{cm^3}}$$

$$\frac{V}{\mathcal{N}} = \frac{4\pi}{3} r_s^3 \qquad r_s = \left(\frac{3V}{4\pi\mathcal{N}}\right)^{\frac{1}{3}}$$

r_s = 1.72 Å (Li), 2.08 Å (Na), 1.12 Å (Fe)

Na$^+$ *radius* = 0.95 Å

$$\left(\frac{r_s}{0.95}\right)^3 > 10$$

$$\varepsilon_m = \frac{mv_m^2}{2} = \frac{3}{2} k_B T$$

$$v_m = 10^7\, cm/s$$

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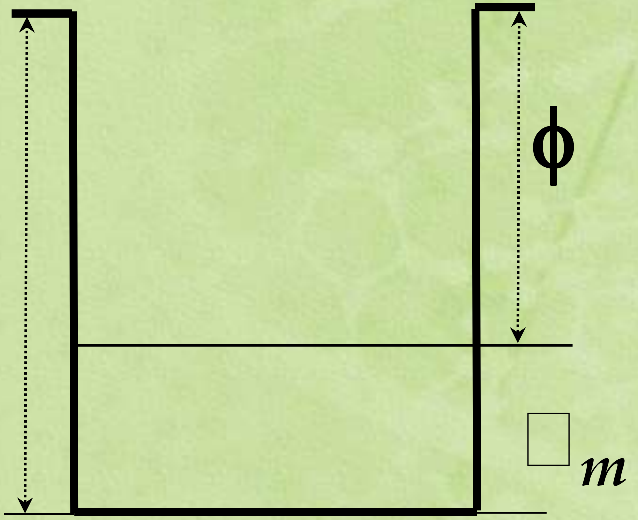

Let see what happens when QM is applied

Main Assumption:

independent electron approximation

$V(\mathbf{r})$ = constant

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi = E\psi \qquad -\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$\frac{\hbar^2}{2m}k^2\psi = E\psi \qquad E = \frac{\hbar^2}{2m}k^2 \qquad \psi = Ae^{i\vec{k}\cdot\vec{r}}$$

$$\psi = Ae^{i\vec{k}\cdot\vec{r}}$$

$$\hat{p}\psi \equiv -i\hbar\frac{\partial}{\partial r}\psi = -i\hbar\frac{\partial}{\partial r}\left(Ae^{i\vec{k}\cdot\vec{r}}\right) = \hbar\vec{k}\psi$$

De Broglie relation states that

$$p = \frac{h}{\lambda}$$

$$k = \left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

Two kinds of boundary conditions

$$\psi(0)=\psi(L)=0$$

$$\psi_n=\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{n\pi x}{L}\right)$$

$$E_n=\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2$$

$$\psi(x) = \psi(x+L)$$

$$\psi(x) = Ae^{ik_x x} \qquad \psi(x+L) = Ae^{ik_x x}e^{ik_x L} \qquad e^{ik_x L} = 1$$

$$k_x L = 2\pi\bar{m}$$

$$\psi_{\bar{m}}(x) = L^{-\frac{1}{2}}e^{i\frac{2\pi\bar{m}x}{L}}$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi\bar{m}}{L}\right)^2$$

$$\bar{m} = 0, \pm 1, \pm 2, \ldots$$

Moving to three dimensions

$$\psi_{\bar{m}}\left(x,y,z\right)=L^{-\frac{3}{2}}e^{i\left(\frac{2\pi}{L}\right)\left(\bar{m}_x x+\bar{m}_y y+\bar{m}_z z\right)}$$

$$E_{\bar{m}}=\frac{\hbar^2}{2m}k^2=\frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(\bar{m}_x^2+\bar{m}_y^2+\bar{m}_z^2\right)$$

$$\bar{m}_x,\bar{m}_y,\bar{m}_z=0,\pm1,\pm2,\ldots$$

$$\vec{k}=\frac{2\pi}{L}\vec{\bar{m}}$$

$$\vec{k} = \frac{2\pi}{L}\vec{\bar{m}}$$

$$\psi_{\bar{m}}(x,y,z) = L^{-\frac{3}{2}} e^{i\left(\frac{2\pi}{L}\right)\left(\bar{m}_x x + \bar{m}_y y + \bar{m}_z z\right)}$$

$$\psi_k = V^{-\frac{1}{2}} e^{i\vec{k}\cdot\vec{r}}$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(\bar{m}_x^2 + \bar{m}_y^2 + \bar{m}_z^2\right)$$

$$E_{\bar{m}} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

Degeneracies of free electron levels

Typical possibilities				Orbital degeneracy	Total degeneray
$\bar{m}_x$	$\bar{m}_y$	$\bar{m}_z$	$\bar{m}^2$		
0	0	0	0	1	2
±1	0	0	1	6	12
±1	±1	0	2	12	24
±1	±1	±1	3	8	16
±2	0	0	4	6	12

For large m values the degeneracies go up as $\left(\bar{m}^2\right)^{\frac{1}{2}}$

$$\bar{m}_F = \left|\vec{\bar{m}}_{\max}\right|$$

Energy, temperature and velocity of electrons with m_F

$$\hat{p}\psi \equiv -i\hbar\frac{\partial}{\partial r}\psi = -i\hbar\frac{\partial}{\partial r}\left(Ae^{i\vec{k}\cdot\vec{r}}\right) = \hbar\vec{k}\psi$$

$$N = 2\left(\frac{4\pi}{3}\right)\bar{m}_F^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k_F^3$$

$$\vec{k} = \frac{2\pi}{L}\vec{\bar{m}}$$

$$E_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\bar{m}_F^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

If we assume that the number of electrons per unit volume is ρ_0, then the Fermi momentum p_F of a uniform free electron gas is:

$$E_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

$$p_F = \hbar\left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$\rho_0 = \frac{N}{V} = \frac{p_F^3}{3\pi^2 h^3}$$

Thomas and Fermi applied such a relation to an inhomogeneous situation as that of atoms, molecules and solids. If the inhomogeneous electron density is denoted by $\rho(\vec{r})$, when the equation defining ρ_0 is applied locally at $\vec{r}$, it yields

$$\rho(\vec{r}) = \frac{p_F^3(\vec{r})}{3\pi^2\hbar^3}$$

Let us define the density of states $g(\varepsilon)$, i.e. the number of states between □ε and $\varepsilon + d\varepsilon$

The number of states with energy up to ε is

$$2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}} \qquad E_F = \frac{\mathrm{h}^2}{2m}k_F^2$$

$$\int_0^{\varepsilon} g(\varepsilon)d\varepsilon = 2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}}$$

$$\int_0^{\varepsilon} g(\varepsilon)\,d\varepsilon = 2\left(\frac{4\pi}{3}\right)\bar{m}^3 = 2\left(\frac{4\pi}{3}\right)\frac{V}{(2\pi)^3}k^3 = \left(\frac{V}{3\pi^2}\right)\left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}}$$

$$g(\varepsilon) = \frac{3}{2}\left(\frac{V}{3\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}} = \sqrt{2}\left(\frac{V}{\pi^2}\right)\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}} = C\varepsilon^{\frac{1}{2}}$$

T_0 = total kinetic energy

$$T_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\,d\varepsilon = C\int_0^{\varepsilon_F} \varepsilon^{\frac{3}{2}}\,d\varepsilon = \frac{2}{5}C\varepsilon_F^{\frac{5}{2}}$$

$$p_F = \hbar\left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

$$\left(\varepsilon_F\right)^{\frac{3}{2}} = \left(\frac{\hbar^2}{2m}\right)^{\frac{3}{2}}\left(\frac{3\pi^2 N}{V}\right)$$

$$T_0 = \frac{2}{5}C\varepsilon_F^{\frac{5}{2}} = \frac{2}{5}\underbrace{\sqrt{2}\left(\frac{V}{\pi^2}\right)\left(\frac{m}{h^2}\right)^{\frac{3}{2}}}_{C}\left(\frac{h^2}{2m}\right)^{\frac{3}{2}}\left(\frac{3\pi^2 N}{V}\right)\varepsilon_F = \frac{3}{5}N\varepsilon_F$$

$$T_0 = \frac{3}{5} N \varepsilon_F \qquad\qquad T_0 = \frac{2}{5} C \varepsilon_F^{\frac{5}{2}}$$

$$T_0\left[\rho_0\right] = \frac{2}{5} \underbrace{\sqrt{2}\left(\frac{V}{\pi^2}\right)\left(\frac{m}{\hbar^2}\right)^{\frac{3}{2}}}_{C} \underbrace{\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{\frac{2}{3}} \rho_0^{\frac{2}{3}}\right)}_{\varepsilon_F}^{\frac{5}{2}}$$

$$T_0\left[\rho_0\right] = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} V \rho_0^{\frac{5}{3}} \qquad T\left[\rho(\vec{r})\right] = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} V \rho(\vec{r})^{\frac{5}{3}}$$

One can next write the classical energy equation for the fastest electrons as

$$\mu = \frac{p_F^2(\vec{r})}{2m} + V(\vec{r})$$

$$\rho(\vec{r}) = \frac{p_F^3(\vec{r})}{3\pi^2\hbar^3} \qquad \mathrm{h}\left(3\pi^2\right)^{\frac{1}{3}}\left\{\rho\left(\overset{\mathrm{r}}{r}\right)\right\}^{\frac{1}{3}} = p_F\left(\overset{\mathrm{r}}{r}\right)$$

$$\mu = \left(\frac{\hbar^2}{2m}\right)\left(3\pi^2\right)^{\frac{2}{3}}\left\{\rho(\vec{r})\right\}^{\frac{2}{3}} + V(\vec{r})$$

The basic equation of the TF theory. It is a classical expression, and consequently it can be applied only in those cases for which μ – V > 0

$$T\left[\rho(\vec{r})\right]=\frac{3h^{2}}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}}\mathrm{l}^{3}\rho(\vec{r})^{\frac{5}{3}}$$

$$T_{TF}\left[\rho(\vec{r})\right]=C_{TF}\int\rho^{\frac{5}{3}}(\vec{r})d\vec{r}$$

$$E_{TF}\left[\rho(\vec{r})\right]=C_{TF}\int\rho^{\frac{5}{3}}(\vec{r})d\vec{r}-Z\int\frac{\rho(\vec{r})}{\vec{r}}d\vec{r}+\frac{1}{2}\iint\frac{\rho(\vec{r}_{1})\rho(\vec{r}_{2})}{\left|\vec{r}_{1}-\vec{r}_{2}\right|}d\vec{r}_{1}d\vec{r}_{2}$$

A results of the free electron gas theory is that the mean kinetic energy per particle is 3/5 of the Fermi energy. The total kinetic energy T_0 of a free electron gas constituted by N particles is then:

$$T_0 = \tfrac{3}{5}\left(\frac{p_F^2}{2m}\right)N$$

and hence, t_0 (the kinetic energy per unit volume) is

$$t_0 = \frac{T_0}{V} = \frac{3}{5}\left(\frac{p_f^2}{2m}\right)\rho_0 = C_k\rho_0^{5/3}, \qquad C_k = \tfrac{3\hbar^2}{10m}\left(3\pi^2\right)^{2/3}$$

$$t = C_k \left\{\rho(\vec{r})\right\}^{5/3}$$

$$E = C_k \int \left\{\rho(\vec{r})\right\}^{5/3} d\vec{r} + \int \rho(\vec{r}) V_M(\vec{r}) d\vec{r} + \frac{e^2}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}\,')}{\left|\vec{r} - \vec{r}\,'\right|} d\vec{r}\, d\vec{r}\,'$$

The physical meaning of the last equation is that the electronic properties of a system are determined as functionals of the electronic density by applying, locally, relations appropriate to a homogeneous free electron gas. This approximation, known as local density approximation (LDA), is probably one of the most important concept of the modern DFT!

$$N = N\left[\rho(\vec{r})\right] = \int \rho(\vec{r})\,d\vec{r}$$

$$\delta\left\{E_{TF}[\rho] - \mu_{TF}\left(\int \rho(\vec{r})\,d\vec{r} - N\right)\right\} = 0$$

$$\mu_{TF} = \frac{\delta E_{TF}[\rho]}{\delta\rho(\vec{r})} = \tfrac{5}{3}C_F\,\rho^{\frac{2}{3}}(\vec{r}) - \Phi(\vec{r})$$

$$\Phi(\vec{r}) = \frac{Z}{r} - \int \frac{\rho(\vec{r}_2)}{\left|\vec{r} - \vec{r}_2\right|}\,d\vec{r}_2$$

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$$\hat{v}_X^{HF} \approx v_{X\alpha}\left(\left[\rho(\vec{r})\right];\vec{r}\right) = -\tfrac{3}{2}\alpha\left[\tfrac{3}{\pi}\rho(\vec{r})\right]^{\frac{1}{3}}$$

A *non local* operator is characterized by the general equation

$$\langle \vec{r}\,' | \hat{A} | \Psi \rangle = \int d\vec{r}\, \hat{A}\left(\vec{r}\,', \vec{r}\right) \Psi(\vec{r}) = \Psi'\left(\vec{r}\,'\right) \qquad \hat{A}\left(\vec{r}\,', \vec{r}\right) = \langle \vec{r}\,' | \hat{A} | \vec{r} \rangle$$

$$\langle \vec{r}\,' | \hat{A} | \vec{r} \rangle = \hat{A}(\vec{r})\,\delta\left(\vec{r}\,' - \vec{r}\right)$$

The Kohn-Sham method

$$T = \sum_{i=1}^{N} q_i \left\langle \psi_i \middle| -\tfrac{1}{2}\nabla^2 \middle| \psi_i \right\rangle$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} q_i \sum_{s} \left| \psi_i(\vec{r}, s) \right|^2$$

$$T_s = \sum_{i=1}^{N} \left\langle \psi_i \middle| -\tfrac{1}{2}\nabla^2 \middle| \psi_i \right\rangle$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \sum_{s} \left| \psi_i(\vec{r}, s) \right|^2$$

In ogni punto si associa alla densita alla densita $\rho(\mathbf{r})$ *l'energia XC che avrebbe un gas elettronico uniforme con la stessa densità. Ciò è ripetuto per ogni punto e i valori usati nelle formule*

QuickTime™ and a
decompressor
are needed to see this picture.

The seven majar kings of science

Theodor
von Kàrmàn

George
de Hevesy

Michael
Polanyi

Leo Szilard

Eugene
Wigner

John
von Neumann

Edward
Teller

QuickTime™ and a
decompressor
are needed to see this picture.

QuickTime™ and a
decompressor
are needed to see this picture.

P. Hohenberg

W. Kohn

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \tfrac{1}{2} \sum_{i,j=1}^{N} \left(J_{ij} - K_{ij} \right)$$

$$H_i = \int \psi_i^*(\mathbf{x}) \left[-\tfrac{1}{2} \nabla^2 + v(\mathbf{x}) \right] \psi_i(\mathbf{x}) d\mathbf{x}$$

$$J_{ij} = \iint \psi_i(\mathbf{x}_1) \psi_i^*(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$K_{ij} = \iint \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

Minimization and orthonomalization conditions

$$\hat{F}\psi_i(\mathbf{x}) = \sum_{j=1}^{N} \varepsilon_{ij}\psi_j(\mathbf{x})$$

$$\hat{F} = -\tfrac{1}{2}\nabla^2 + v + \hat{g}$$

Background

- 1920s: **Introduction of the Thomas-Fermi model.**
- 1964: **Hohenberg-Kohn paper proving existence of exact DF.**
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA. DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello) (Now one of PRL's top 10 cited papers).
- 1988: Becke and LYP functionals. DFT useful for some chemistry.
- 1998: Nobel prize awarded to Walter Kohn in chemistry for development of DFT.

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decompressor
are needed to see this picture.

The first HK theorem legitimates ρ as basic variable.

The external potential is determined, within a trivial additive constant, by the electron density.

$$E_v[\rho]=T[\rho]+V_{em}[\rho]+V_{ee}[\rho]=\int\rho(\vec{r})v(\vec{r})d\vec{r}+F_{HK}[\rho]$$

$$F_{HK}[\rho]=T[\rho]+V_{ee}[\rho]$$

$$V_{ee}[\rho]=J[\rho]+\text{non classical terms}$$

The second HK theorem supplies the variational principle for the ground state energy.

$$\int \tilde{\rho}(\vec{r})d\vec{r} = N \qquad E_0 \le E_v\left[\tilde{\rho}\right]$$

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

The ground state energy and density correspond to the minimum of some functional E_ν subject to the constraint that the density contains the correct number of electrons. The Lagrange multiplier of this constraint is the electronic chemical potential μ.

In matematica e in fisica teorica, la derivata funzionale è una generalizzazione della derivata direzionale. La differenza è che la seconda differenzia nella direzione di un vettore, mentre la prima differenzia nella direzione di una funzione. Entrambe possono essere viste come estensioni dell'usuale derivata.

$$F[\rho] = \int f\left(\vec{r}, \rho, \nabla\rho, \nabla^2\rho, \ldots\right) d^3r$$

$$\frac{\delta F[\rho]}{\delta\rho} = \frac{\delta f}{\delta\rho} - \nabla \cdot \frac{\delta f}{\delta(\nabla\rho)} + \nabla^2 \frac{\delta f}{\delta(\nabla^2\rho)} - \ldots$$

$$J[\rho]=\frac{1}{2}\int\left(\frac{\rho(\vec r)\rho(\vec r\,')}{|\vec r-\vec r\,'|}d^3r'\right)d^3r$$

$$\frac{\delta J[\rho]}{\delta\rho}=\frac{\delta j}{\delta\rho}=\int\frac{\rho(\vec r\,')}{|\vec r-\vec r\,'|}d^3r'$$

$$j=\frac{1}{2}\int\frac{\rho(\vec r)\rho(\vec r\,')}{|\vec r-\vec r\,'|}d^3r'$$

$$\frac{\delta^2 J[\rho]}{\delta\rho^2}=\frac{\delta}{\delta\rho}\int\frac{\rho(\vec r\,')}{|\vec r-\vec r\,'|}d^3r'=\frac{\delta}{\delta\rho}\frac{\rho(\vec r\,')}{|\vec r-\vec r\,'|}=\frac{1}{|\vec r-\vec r\,'|}$$

$$E_v[\rho] = T[\rho] + V_{em}[\rho] + V_{ee}[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + F_{HK}[\rho]$$

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(\vec{r})} = v(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta\rho(\vec{r})}$$

Despite the importance of the HK theorems, it is noteworthy that the result they give is somehow incomplete. Actually, the first HK theorem refers only to the ground state energy and ground state density. Furthermore, as far as the second HK theorem is concerned, it is *simply* an existence theorem and no information about how to get the ground state energy functional is provided. Nevertheless, the existence of an exact theory justifies the research of new funtionals that, though approximate version of the correct one, are more and more accurate.

Background

- 1920s: **Introduction of the Thomas-Fermi model.**
- 1964: **Hohenberg-Kohn paper proving existence of exact DF.**
- 1965: **Kohn-Sham scheme introduced.**
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The Kohn-Sham method.

The massive usage of DFT is tightly bound to its use in orbitalic theories. This is not very surprising because of the role played by these theories, in particular the HF one, in quantum chemistry. Thus, the major DFT developments have implied either the improvement of existing orbitalic theories, for instance the Xα method [Slater, 1951a-b], or the proposal of new approaches [Kohn & Sham, 1965].

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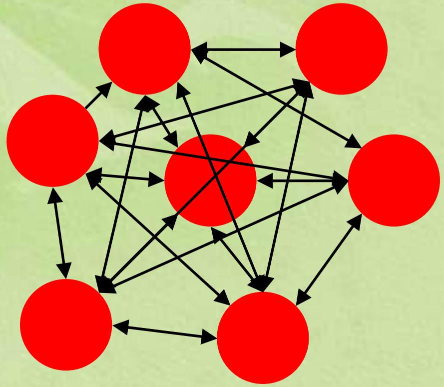
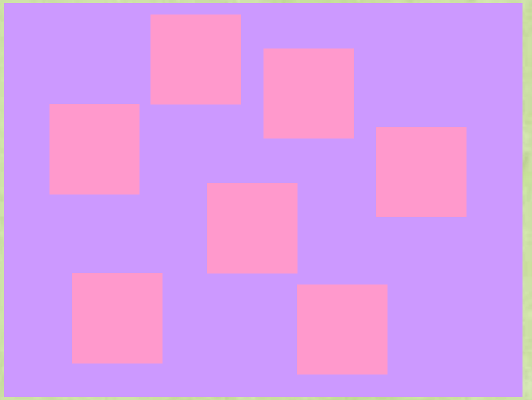




Interacting electrons
+ real potential

Non-interacting fictitious
particles + effective potential

$$\hat{H}_s = \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_i^N v_s\left(\vec{r}_i\right)$$

$$\Psi_s = \frac{1}{\sqrt{N!}} \det\left[\psi_1\psi_2\cdots\psi_N\right]$$

$$\hat{h}_s\psi_i = \left[-\tfrac{1}{2}\nabla^2 + v_s\left(\vec{r}\right)\right]\psi_i = \varepsilon_i\psi_i$$

$$T_s\left[\rho\right] = \left\langle \Psi_s \left| \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) \right| \Psi_s \right\rangle = \sum_i^N \left\langle \psi_i \left| -\tfrac{1}{2}\nabla^2 \right| \psi_i \right\rangle$$

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \qquad J[\rho] = \tfrac{1}{2}\iint \tfrac{1}{r_{12}}\rho(\vec{r}_1)\rho(\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2$$

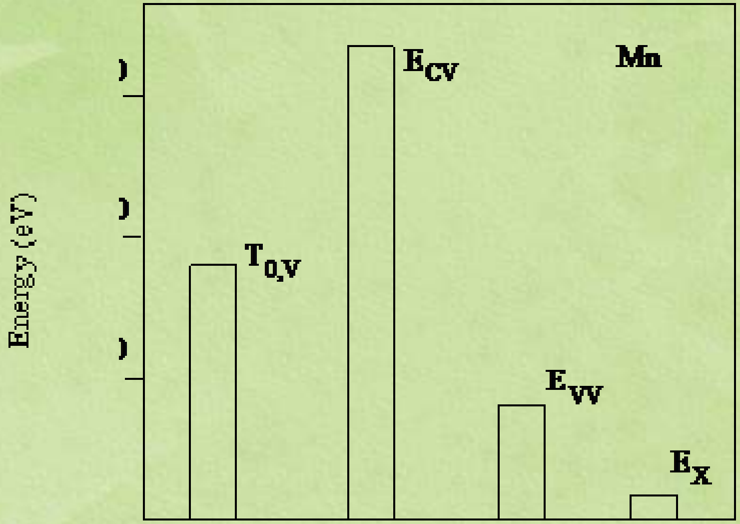
$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(\vec{r})} = v(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta\rho(\vec{r})} \qquad \mu = v_{eff}(\vec{r}) + \frac{\delta T_s[\rho]}{\delta\rho(\vec{r})}$$

$$v_{eff}(\vec{r}) = v(\vec{r}) + \frac{\delta J[\rho]}{\delta\rho(\vec{r})} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} = v(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\,d\vec{r}\,' + v_{xc}(\vec{r})$$

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

With reference to the single Euler - Lagrange equation, the introduction of N orbitals allows us to treat exactly T_s, the dominant part of the true kinetic energy $T[\rho]$. The cost we have to pay is the needed of N equations rather than one expressed in terms of the total electron density. The KS equations have the same form of the Hartree equations unless the presence of a more general local potential, $v_{eff}\left(\vec{r}\right)$. The computational effort for their solution is comparable to that required for the Hartree equations and definitely smaller than that pertinent to the HF ones. HF equations are characterized by a one-electron Hamiltonian including a non local potential and for this reason they cannot be considered a special case of the KS equations.



Relative magnitudes of contributions to total valence energy (in eV) of the Mn atom

The exchange-correlation potential

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons.

Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly.

A common approximation is the so-called local density approximation (LDA) which locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density.

The Local Density Approximation (LDA)

The LDA approximation assumes that the density is slowly varying and the inhomogeneous density of a solid or molecule can be calculated using the homogeneous electron gas functional.

While many ground state properties (lattice constants, bulk moduli, etc.) are well described in the LDA, the dielectric constant is overestimated by 10-40% in LDA compared to experiment. This overestimation stems from the neglect of a polarization-dependent exchange correlation field in LDA compared to DFT.

The method can be improved by including the gradient of the density into the functional. The generalized gradient approximation GGA is an example of this type of approach.

The Slater exchange functional

The predecessor to modern DFT is Slater's Xα method. This method was formulated in 1951 as an approximate solution to the Hartree-Fock equations. In this method the HF exchange was approximated by:

$$E_{X\alpha}[\rho] = -\frac{9}{4}\alpha\left(\frac{3}{4\pi}\right)^{1/3}\int_0^\infty \rho^{4/3}(r)dr$$

The exchange energy $E_{X\alpha}$ is a fairly simple function of the electron density ρ.

The adjustable parameter α was empirically determined for each atom in the periodic table. Typically α is between 0.7 and 0.8. For a free electron gas $\alpha = 2/3$.

The VWN Correlation Functional

In ab initio calculations of the Hartree-Fock type electron correlation is also not included. However, it can be included by inclusion of configuration interaction (CI). In DFT calculations the correlation functional plays this role. The Vosko-Wilk-Nusair correlation function is often added to the Slater exchange function to make a combination exchange-correlation functional.

$E_{xc} = E_x + E_c$

The nomenclature here is not standardized and the correlation functionals themselves are very complicated functions. The correlation functionals can be seen on the MOLPRO website http://www.molpro.net/molpro2002.3/doc/manual/node146.html.

Application of the LDA

Application of LDA methods to semi-conductor materials and insulators gives good agreement for the lattice constant and bulk modulus.

The lattice constants are typically accurate to within 1-2% up the second row in the periodic table. Since the crystal volume V is accurately calculated the density is, of course, also obtained.

The bulk modulus is:

$$B = -V\left(\frac{\partial P}{\partial V}\right) = -V\left(\frac{\partial^2 E}{\partial V^2}\right)$$

Bulk moduli are calculated by systematically varying the lattice parameters and plotting the energy as a function of V. The curvature at the minimum of the E(V) plot is proportional to the lattice constant.

Extensions of the LDA approach

Generalized gradient approximation (GGA). Take density gradient into account. Useful for molecules.

Spin density functional theory. Two independent variables: density and magnetization.

$$m(r) = -\mu_0\left(\rho_\uparrow - \rho_\downarrow\right)$$

Exact exchange density functional theory. Calculate exchange exactly and correlation approximately using DFT.

Generalized density functional theory. Modify K-S energy partitioning to obtain a non-local hamiltonian.

Generalized Gradient Approach (GGA)

The GGA approach takes into account variations in the density by including the gradient of the density in the functional. One commonly used GGA functional is that of Becke.

$$V_{xc}^{B} = -\beta\rho^{1/3}\frac{x^2}{\left(1 + 6\beta x \sinh^{-1} x\right)} \quad , x = \frac{\nabla\rho}{\rho^{4/3}}$$

This functional has only one adjustable parameter, β. The value of $\beta = 0.0042$ was determined based on the best fit to the energies of six noble gas atoms using the sum of the LDA and GGA exchange terms.

The GGA option in DMol3 is that of Perdew and Wang.

Lee-Yang-Parr Correlation Functional

As was discussed above for the Slater exchange functional (no gradient), the VWN correlation functional provides a significant improvement in the calculation of the energies and properties such as bulk modulus, vibrational frequencies etc. In a similar manner the Becke exchange functional (including a gradient correlation) and the Lee-Yang-Parr functional are used together. The Lee-Yang-Parr or LYP correlation functional is quite complicated. It can be viewed on the MOLPRO website.

Thus, two of the most commonly used functionals are:
S-VWN Slater exchange - VWN correlation (no gradients)
B-LYP Becke exchange - LYP correlation (gradients)

Integrated Computational Materials Engineering Education

Lecture on Density Functional Theory

An Introduction

Mark Asta
Department of Materials Science and Engineering
University of California, Berkeley
Berkeley, CA 94720

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- The Division of Materials Research at the National Science Foundation is acknowledged for financial support in the development of the lecture and module

Use of DFT in Materials Research

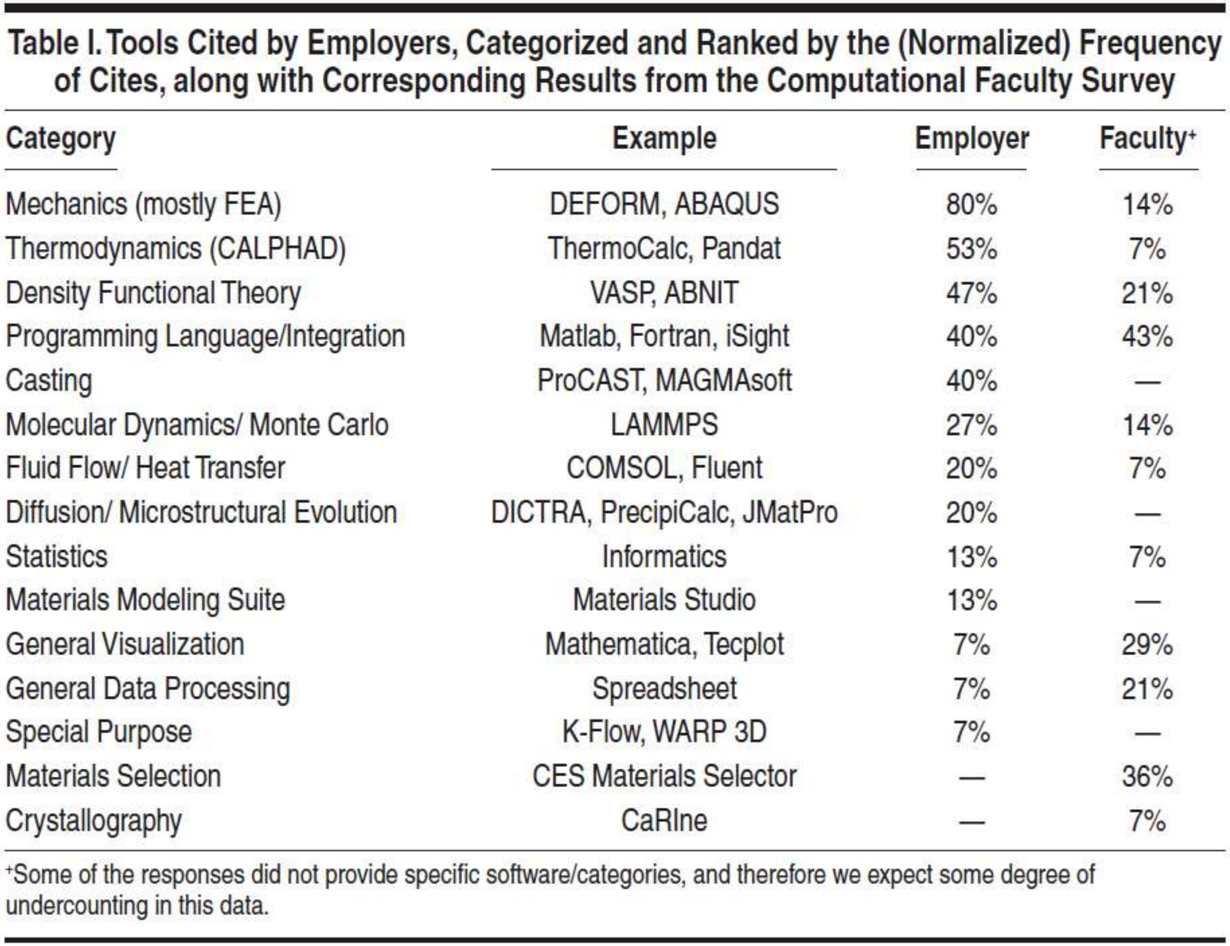


Table I. Tools Cited by Employers, Categorized and Ranked by the (Normalized) Frequency of Cites, along with Corresponding Results from the Computational Faculty Survey

Category	Example	Employer	Faculty+
Mechanics (mostly FEA)	DEFORM, ABAQUS	80%	14%
Thermodynamics (CALPHAD)	ThermoCalc, Pandat	53%	7%
Density Functional Theory	VASP, ABNIT	47%	21%
Programming Language/Integration	Matlab, Fortran, iSight	40%	43%
Casting	ProCAST, MAGMAsoft	40%	—
Molecular Dynamics/ Monte Carlo	LAMMPS	27%	14%
Fluid Flow/ Heat Transfer	COMSOL, Fluent	20%	7%
Diffusion/ Microstructural Evolution	DICTRA, PrecipiCalc, JMatPro	20%	—
Statistics	Informatics	13%	7%
Materials Modeling Suite	Materials Studio	13%	—
General Visualization	Mathematica, Tecplot	7%	29%
General Data Processing	Spreadsheet	7%	21%
Special Purpose	K-Flow, WARP 3D	7%	—
Materials Selection	CES Materials Selector	—	36%
Crystallography	CaRIne	—	7%

+Some of the responses did not provide specific software/categories, and therefore we expect some degree of undercounting in this data.

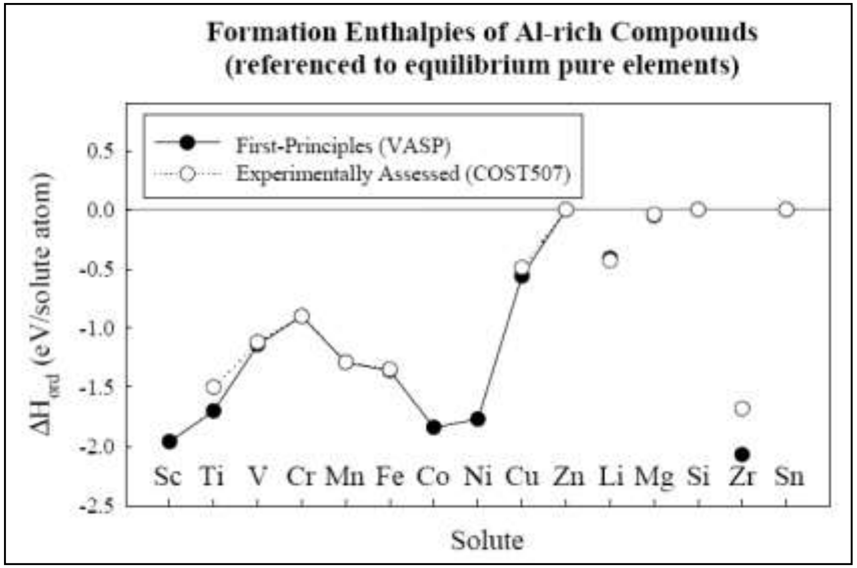
K. Thornton, S. Nola, R. E. Garcia, MA and G. B. Olson, "*Computational Materials Science and Engineering Education: A Survey of Trends and Needs*," JOM (2009)

The Role of Electronic Structure Methods in ICME

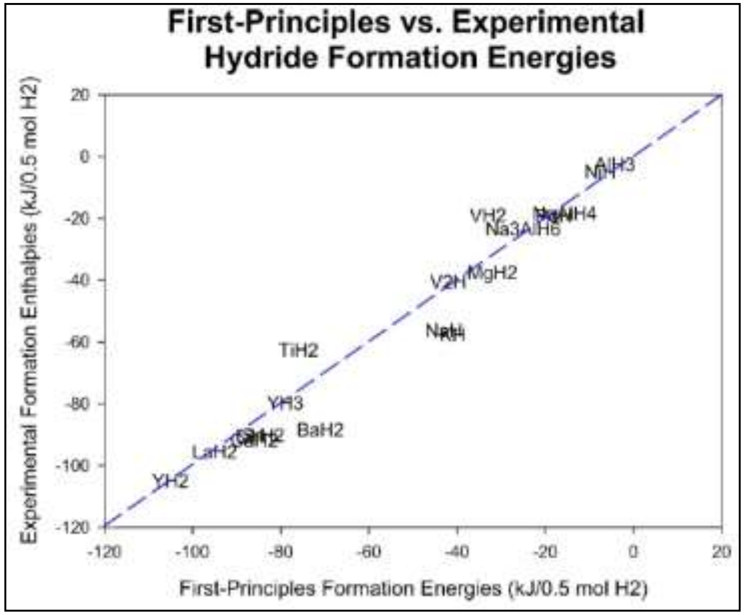
- A wide variety of relevant properties can be calculated from knowledge of atomic numbers alone
  - Elastic constants
  - Finite-temperature thermodynamic and transport properties
  - Energies of point, line and planar defects
- For many classes of systems accuracy is quite high
  - Can be used to obtain “missing” properties in materials design when experimental data is lacking, hard to obtain, or “controversial”
  - Can be used to discover new stable compounds with target properties
- The starting point for “hierarchical multiscale” modeling
  - Enables development of interatomic potentials for larger-scale classical modeling

Accuracy for Some Selected Materials

C. Wolverton and V. Ozolins
(Phys Rev B, 2005)



C. Wolverton, V. Ozolins, MA
(Phys Rev B, 2004)



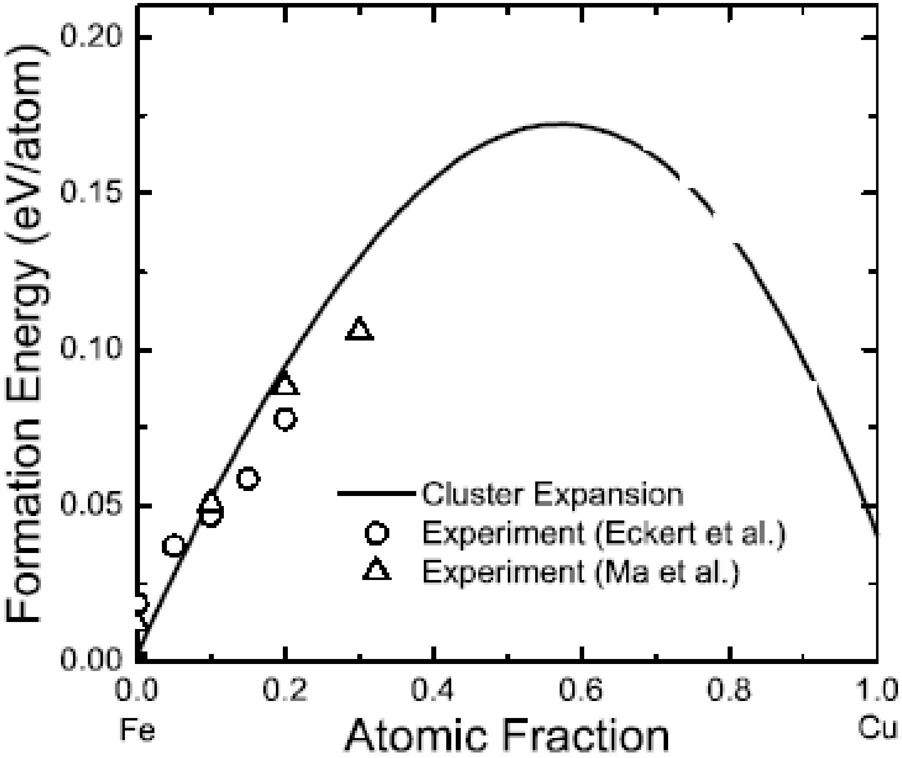
~95 % Success in High Throughput Study Comparing Predicted and Observed Stable Compounds for 80 Binary Systems
S. Curtarolo et al., CALPHAD (2004)

DFT Provides Accurate Framework for Predicting Alloy Phase Stability and Defect Energetics for Wide Range of Alloy Systems

1st-Principles Modeling of Alloy Phase Stability

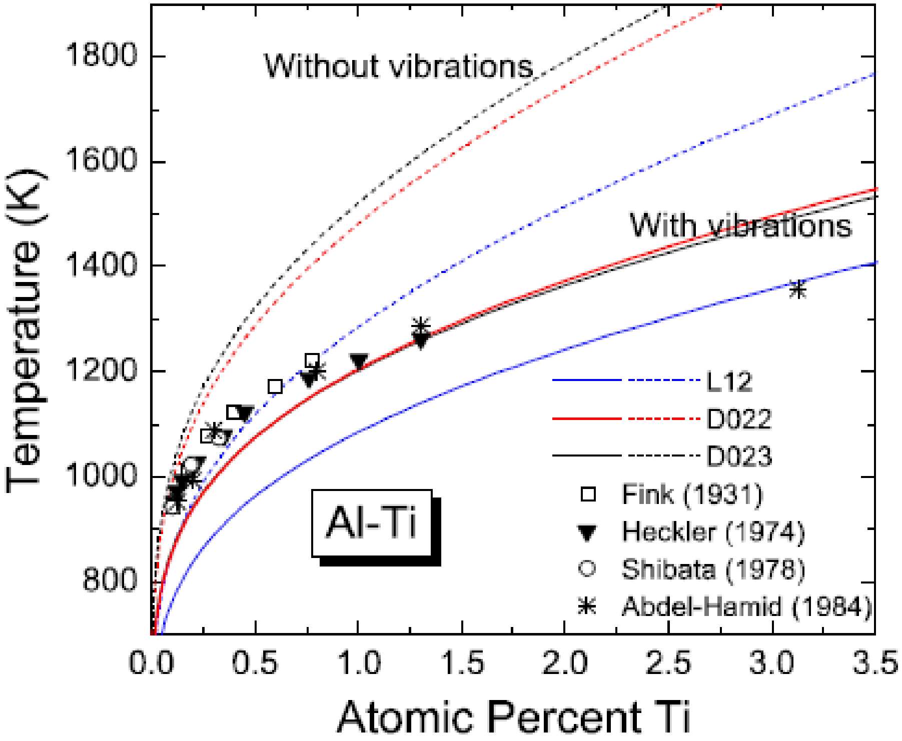
Mixing Energies of BCC Fe-Cu

J. Z. Liu, A. van de Walle, G. Ghosh and MA (2005)



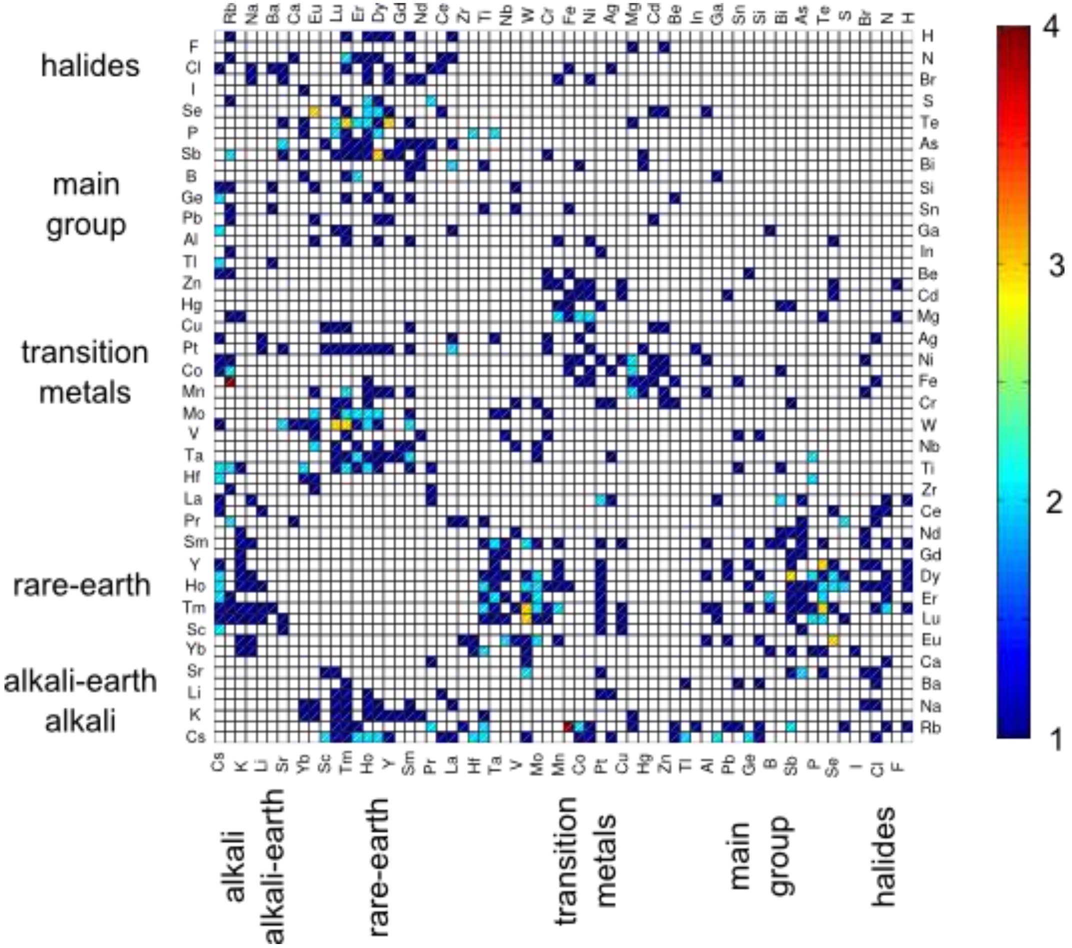
Solvus Boundaries in Al-Ti

J. Z. Liu, G. Ghosh, A. van de Walle and MA (2006)



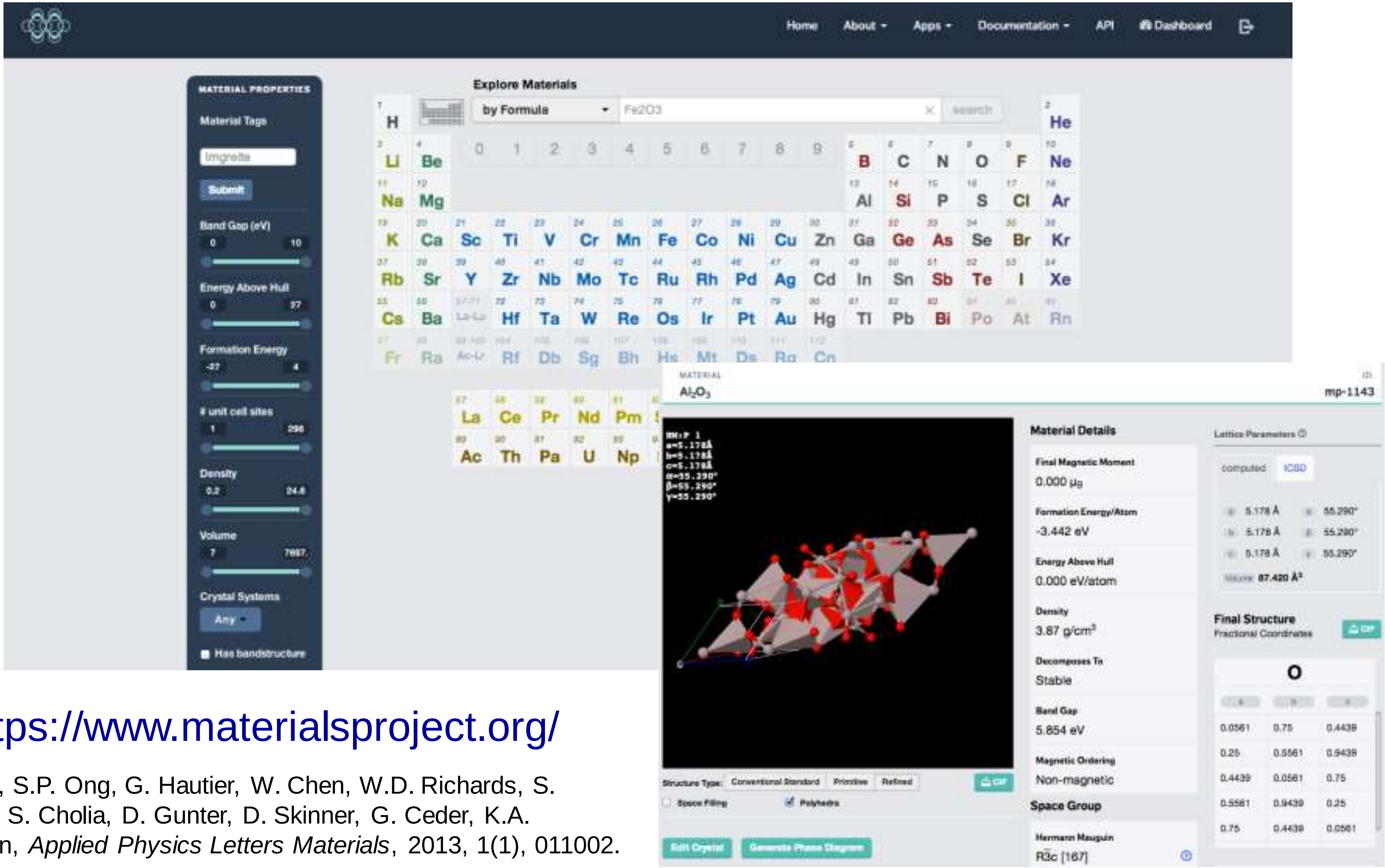
Predictions for Both Stable and *Metastable* Phases

Discovery of New Materials



G. Hautier, C.C. Fischer, A. Jain, T. Mueller, and G. Ceder, “*Finding Nature’s Missing Ternary Oxide Compounds Using Machine Learning and Density Functional Theory*,” Chem. Mater. 22, 3762-3767 (2010)

Materials Data for Discovery & Design



Material Tags: Imgrelta

Band Gap (eV): 0 – 10

Energy Above Hull: 0 – 27

Formation Energy: -27 – 4

unit cell sites: 1 – 296

Density: 0.2 – 24.6

Volume: 7 – 7697.

Crystal Systems: Any

☐ Has bandstructure

Explore Materials — by Formula: Fe2O3

MATERIAL: Al_2O_3

ID: mp-1143

```
RH:P 1
a=5.178Å
b=5.178Å
c=5.178Å
α=55.290°
β=55.290°
γ=55.290°
```

Material Details

Final Magnetic Moment: 0.000 μB

Formation Energy/Atom: -3.442 eV

Energy Above Hull: 0.000 eV/atom

Density: 3.87 g/cm^3

Decomposes To: Stable

Band Gap: 5.854 eV

Magnetic Ordering: Non-magnetic

Space Group

Hermann Mauguin: R$\bar{3}$c [167]

Lattice Parameters

a	5.178 Å	α	55.290°
b	5.178 Å	β	55.290°
c	5.178 Å	γ	55.290°

Volume 87.420 Å^3

Final Structure
Fractional Coordinates

O

x	y	z
0.0561	0.75	0.4439
0.25	0.5561	0.9439
0.4439	0.0561	0.75
0.5561	0.9439	0.25
0.75	0.4439	0.0561

https://www.materialsproject.org/

A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, *Applied Physics Letters Materials*, 2013, 1(1), 011002.

Outline

- Formalism
  - Hydrogen Atom
  - Density Functional Theory
    - Exchange-Correlation Potentials
    - Pseudopotentials and Related Approaches
    - Some Commercial and Open Source Codes
- Practical Issues
  - Implementation
    - Periodic boundary conditions
    - k-Points
    - Plane-wave basis sets
  - Parameters controlling numerical precision
- Example Exercise

Introduction

The Hydrogen Atom

Proton with mass M_1, coordinate $\mathbf{R}_1$
Electron with mass m_1, coordinate $\mathbf{r}_1$

$$\left(-\frac{\hbar^2}{2M_1}\nabla_1^2-\frac{\hbar^2}{2m_2}\nabla_2^2-\frac{e^2}{r}\right)\Psi(R_1,r_2)=E\Psi(R_1,r_2)$$

$$r=r_1-r_2,\qquad R=\frac{M_1R_1+m_2r_2}{M_1+m_2},\qquad m=\frac{M_1m_2}{M_1+m_2},\qquad M=M_1+m_2$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2m}\nabla_r^2-\frac{e^2}{r}\right)\Psi(R,r)=E\Psi(R,r)$$

$$\Psi(R,r)=\psi_{cm}(R)\psi_r(r)$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2\right)\psi_{cm}(R)=E_{cm}\psi_{cm}(R)$$

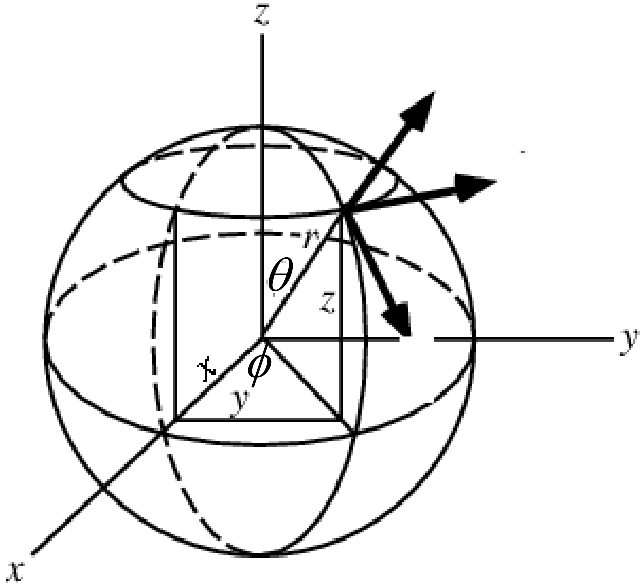
$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla_r^2-\frac{e^2}{r}\right)\psi_r(r)=E_r\psi_r(r)}$$

Hydrogen Atom

Switch to Spherical Coordinates

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right)-\frac{e^2}{r}\psi=E\psi$$

$$\psi(r,\theta,\phi)=R_{nl}(r)Y_l^m(\theta,\phi)$$



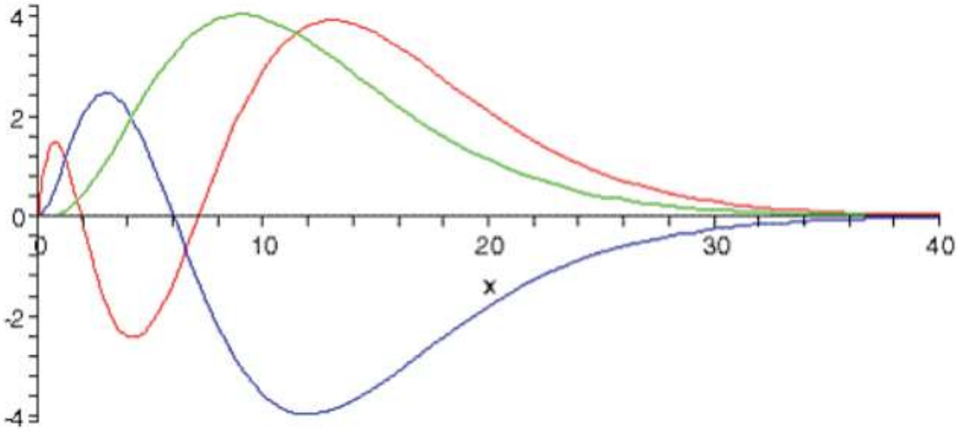
$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)-\frac{l(l+1)}{r^2}-\frac{e^2}{r}\right)R_{nl}(r)=E_nR_{nl}(r)$$

$$E_n=-\frac{me^4}{2\hbar^2}\frac{1}{n^2}=-\frac{13.6}{n^2}\text{eV}$$

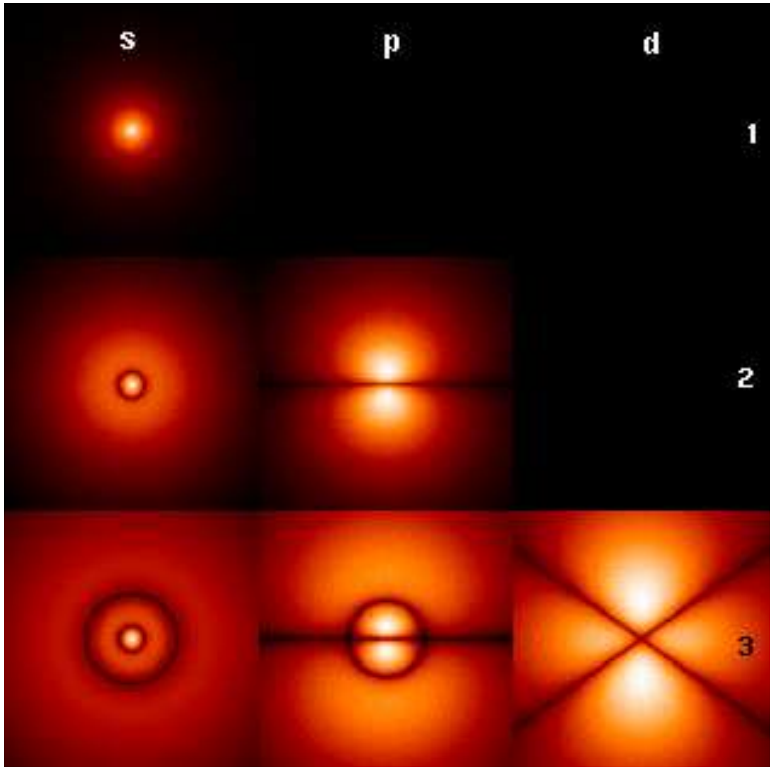
Hydrogen Atom

Wavefunctions

n = 1, 2, 3, …
l = 0 (s), 1(p), 2(d), …, n-1



http://galileo.phys.virginia.edu/classes/751.mf1i.fall02/HydrogenAtom.htm

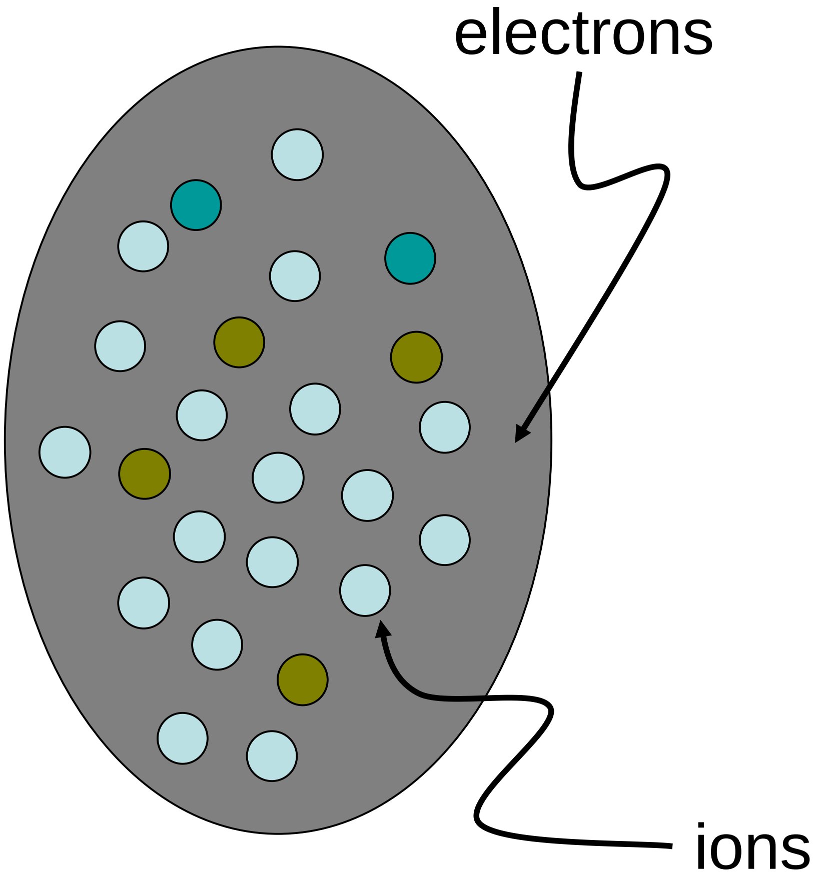


Probability densities through the xz-plane for the electron at different quantum numbers (*l*, across top; n, down side; m = 0)

http://en.wikipedia.org/wiki/Hydrogen_atom

The Many-Electron Problem

- collection of
  - N ions
  - n electrons
- total energy computed as a function of ion positions
  - must employ quantum mechanics



Born-Oppenheimer Approximation

- Mass of nuclei exceeds that of the electrons by a factor of 1000 or more
  - we can neglect the kinetic energy of the nuclei
  - treat the ion-ion interaction classically
  - significantly simplifies the Hamiltonian for the electrons
- Consider Hamiltonian for *n* electrons in potential of *N* nuclei with atomic numbers Z_i

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_i e^2}{\left|\mathbf{R}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\substack{j=1\\ i\neq j}}^{n}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

external potential o $V_{\text{ext}}\left(\mathbf{r}_j\right)$

Density Functional Theory

Hohenberg and Kohn (1964), Kohn and Sham (1965)

- For each external potential there is a unique ground-state electron density
- Energy can be obtained by minimizing of a *density functional with respect to density of electrons n(r)*

$$\boxed{E_{\text{groundstate}}=\min\{E_{\text{tot}}[n(r)]\}}$$

$$E_{\text{tot}}\left[n(\mathbf{r})\right]=\underbrace{T\left[n(\mathbf{r})\right]}_{\text{Kinetic Energy}}+\underbrace{E_{\text{int}}\left[n(\mathbf{r})\right]}_{\text{Electron-Electron Interactions}}+\underbrace{\int d\mathbf{r}\,V_{\text{ext}}(\mathbf{r})\,n(\mathbf{r})}_{\text{Electron-Ion Interactions}}+E_{\text{ion-ion}}$$

Kohn-Sham Approach

$$n(r) = - e \overset{n}{\underset{i=1}{\text{å}}} \left|f_i(r)\right|^2$$

$$E[\{\phi_i\}] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \int \phi_i^* \nabla_i^2 \phi_i d^3 r + \int V_{ext}(r) n(r) d^3 r$$

$$+ \frac{1}{2} \int \frac{n(r) n(r')}{\left|r - r'\right|} d^3 r d^3 r' + E_{xc}[n(r)]$$

Many-Body Electron-Electron Interactions Lumped into $E_{xc}[n(r)]$

"Exchange-Correlation Energy"

Kohn-Sham Equations

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2+V_{nuclei}(r)+\int\frac{n(r')}{\left|r-r'\right|}d^3r'+V_{xc}(r)\right]\phi_i(r)=\varepsilon_i\phi_i(r)$$

$$V_{xc}(r)\equiv\frac{\delta E_{xc}[n(r)]}{\delta n(r)}$$

Local Density Approximation

(e.g., J. P. Perdew and A. Zunger, Phys. Rev. B ***23****, 5048 (1981))*

$$E_{xc}[n(r)] = \int \varepsilon_{xc}^{\mathrm{hom}}(n(r))\,n(r)\,d^3r$$

$\varepsilon_{xc}^{\mathrm{hom}}(n(r)) \rightarrow$ Exchange – Correlation Energy of Homogeneous Electron Gas of Density n(r)

Generalized Gradient Approximation

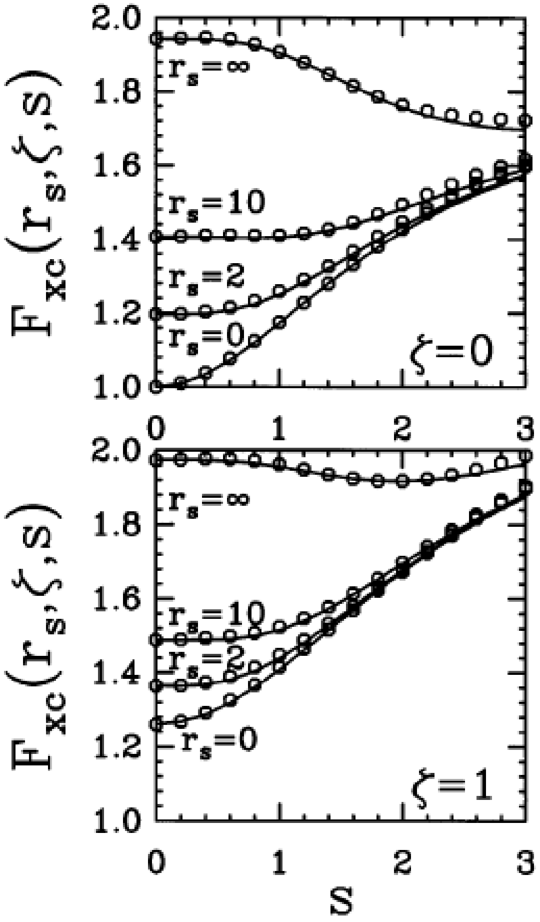
J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77 (1996)

$$E_{xc}^{GGA}[n(r)] = \int \varepsilon_x^{\mathrm{hom}}(n(r))\,n(r)\,F_{xc}(r_s,\zeta,s)\,d^3r$$

$$n = 3/4\pi r_s^3 = k_F^3/3\pi^2$$

$$\zeta = (n_\uparrow - n_\downarrow)/n$$

$$s = |\nabla n|/2k_F n$$

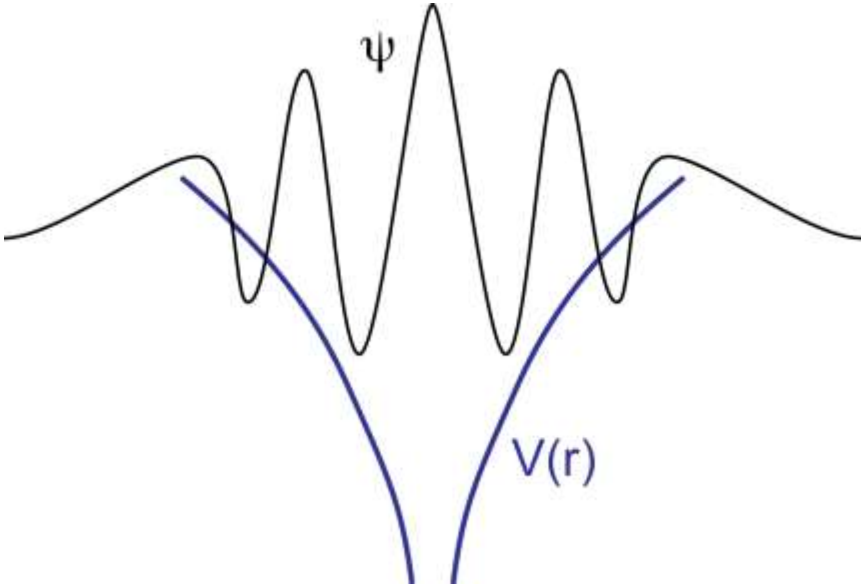


A Note on Accuracy and Ongoing Research

- LDA leads to "overbinding"
  - Lattice constants commonly 1-3 % too small, elastic constants 10-15 % too stiff, cohesive energies 5-20 % too large
- BUT, errors are largely systematic
  - Energy differences tend to be more accurate
- GGA corrects for overbinding
  - Sometimes "overcorrects"
- "Beyond DFT" Approaches
  - For "highly correlated" systems LDA & GGA perform much worse and corrections required (DFT+U, Hybrid Hartree-Fock/DFT, …)
  - Non-bonded interactions, e.g., van der Waals interactions in graphite, require additional terms or functionals (e.g., vdW-DF)

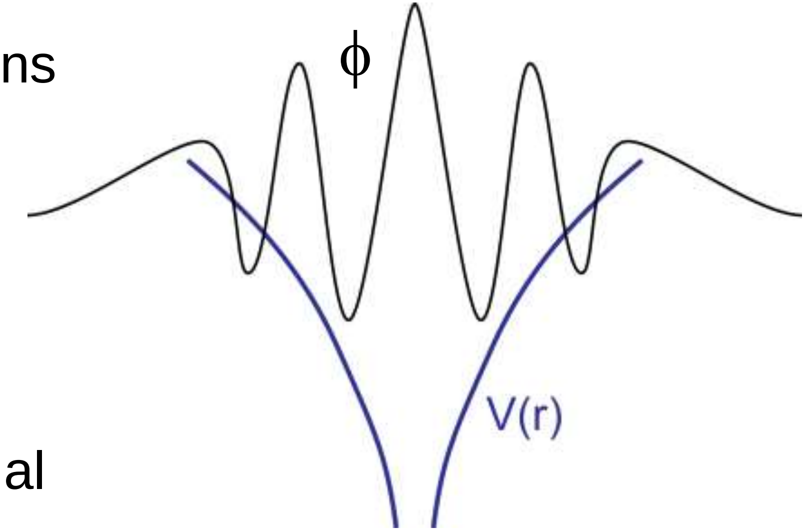
Pseudopotentials

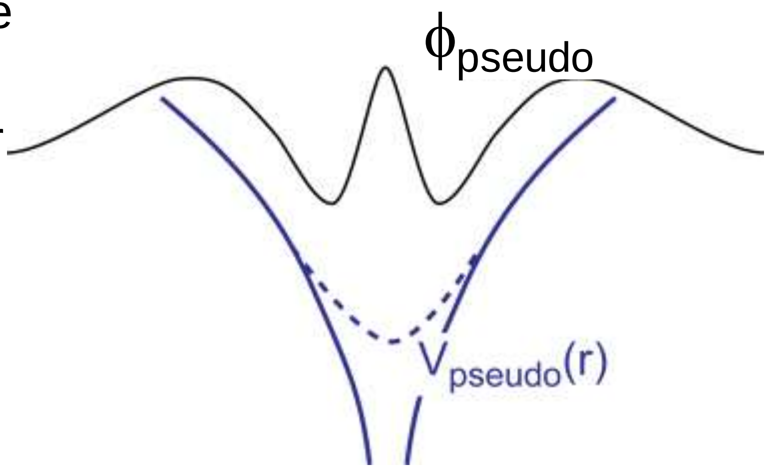
- Potential due to ions is singular at ion core
- Eigenfunctions oscillate rapidly near singularity
- Eigenfunction in bonding region is smooth



Pseudopotentials

- For plane-wave basis sets, rapid oscillations require large number of basis functions
  - expensive
  - unnecessary
    - these oscillations don't alter bonding properties
- Replace potential with nonsingular potential
  - preserve bonding tails of eigenfunction
  - preserve distribution of charge between core and tail regions
  - reduces number of plane waves required for accurate expansion of wavefunction
- Transferable
  - developed from properties of isolated atoms
  - applied in other situations





Summary of Approaches

- Pseudopotentials
  - Core electrons removed from problem and enter only in their effect of the pseudopotential felt by the valence electrons
  - Kohn-Sham equations solved for valence electrons only
- “Augment” Plane Waves with atomic-like orbitals
  - An efficient basis set that allows all electrons to be treated in the calculations
  - Basis for “all-electron” codes
- Projector-Augmented-Wave method
  - Combines features of both methods
  - Generally accepted as the basis for the most accurate approach for calculations requiring consideration of valence electrons only

Some of the Widely Used Codes

- VASP (http://cms.mpi.univie.ac.at/vasp/)
  - Commercial, Plane-Wave Basis, Pseudopotentials and PAW
- PWSCF (http://www.quantum-espresso.org/)
  - Free (and available to run on nanohub), Plane-Wave Basis, Pseudopotentials and PAW
- CASTEP (http://ccpforge.cse.rl.ac.uk/gf/project/castep/)
  - Free in UK, licensed by Accelrys elsewhere, Plane-Wave Basis, Pseudopotentials
- ABINIT (http://www.abinit.org/)
  - Free (and available to run on nanohub), plane-wave basis, pseudopotentials and PAW
- WIEN2K (http://www.wien2k.at/)
  - Commercial (modest license fee), all-electron augmented wave method

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  - Implementation
    - Periodic boundary conditions
    - k-Points
    - Plane-wave basis sets
  - Parameters controlling numerical precision
- Example Exercise

Total Energy in Density Functional Theory

$$E[\{\phi_i\}] = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N_e}\int \phi_i^* \nabla_i^2 \phi_i d^3r + \int V_{ext}(r)n(r)d^3r$$

$$+\frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' + E_{xc}[n(r)]$$

Electron Density $n(r) = -e\sum_{i=1}^{n} |\phi_i(r)|^2$

Electron Wavefunctions $\phi_i(r)$

Potential Electrons Feel from Nuclei $V_{ext}(r)$

Exchange-Correlation Energy $E_{xc}[n(r)]$

Form depends on whether you use LDA or GGA

Kohn-Sham Equations

Schrödinger Equation for Electron Wavefunctions

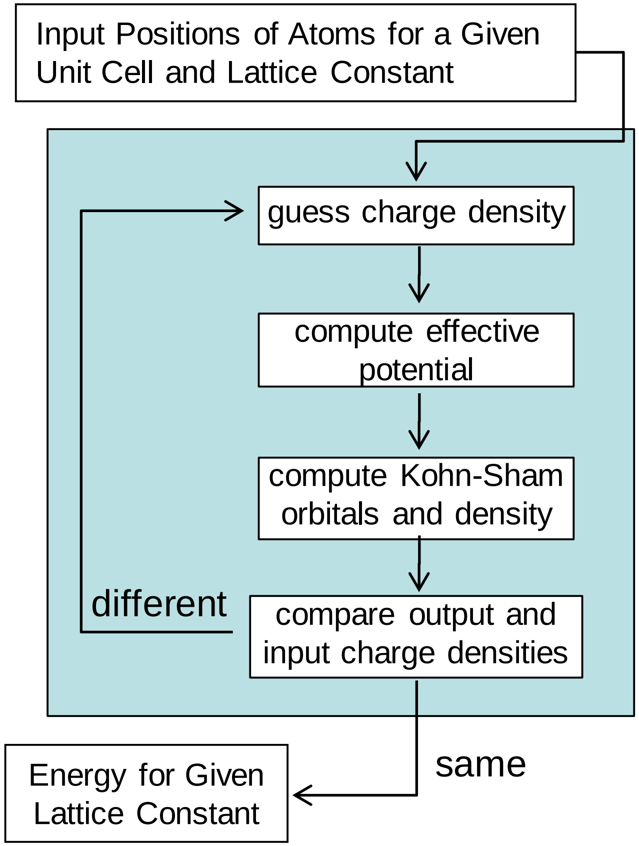
$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2+V_{ext}(r)+\int\frac{n(r')}{|r-r'|}d^3r'+V_{xc}(r)\right]\phi_i(r)=\varepsilon_i\phi_i(r)$$

Exchange-Correlation Potential $V_{xc}(r)\equiv\frac{\delta E_{xc}[n(r)]}{\delta n(r)}$

Electron Density $n(r)=-e\sum_{i=1}^{n}|\phi_i(r)|^2$

Note: ϕ_i depends on *n(r)* which depends on ϕ_i ➔
Solution of Kohn-Sham equations must be done iteratively

Self-Consistent Solution to DFT Equations



Input Positions of Atoms for a Given Unit Cell and Lattice Constant

guess charge density

compute effective potential

compute Kohn-Sham orbitals and density

compare output and input charge densities

different

same

Energy for Given Lattice Constant

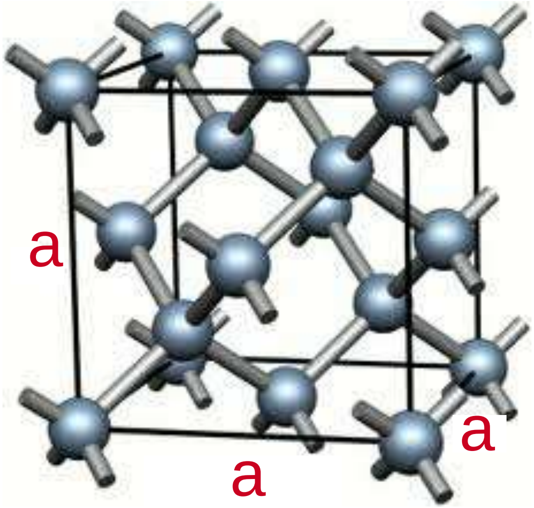
1. Set up atom positions
2. Make initial guess of “input” charge density (often overlapping atomic charge densities)
3. Solve Kohn-Sham equations with this input charge density
4. Compute “output” charge density from resulting wavefunctions
5. If energy from input and output densities differ by amount greater than a chosen threshold, mix output and input density and go to step 2
6. Quit when energy from input and output densities agree to within prescribed tolerance (e.g., 10^{-5} eV)

Note: In your exercise, positions of atoms are dictated by symmetry. If this is not the case another loop must be added to minimize energy with respect to atomic positions.

Implementation of DFT for a Single Crystal

Crystal Structure Defined by Unit Cell Vectors and Positions of Basis Atoms

Example: Diamond Cubic Structure of Si



Unit Cell Vectors

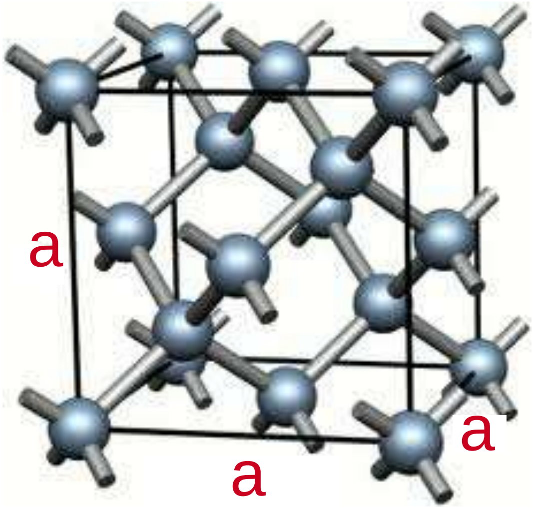
$\mathbf{a}_1$ = a (-1/2, 1/2 , 0)
$\mathbf{a}_2$ = a (-1/2, 0, 1/2)
$\mathbf{a}_3$ = a (0, 1/2, 1/2)

Basis Atom Positions

0 0 0
¼ ¼ ¼

All atoms in the crystal can be obtained by adding integer multiples of unit cell vectors to basis atom positions

Electron Density in Crystal Lattice



Unit-Cell Vectors

$\mathbf{a}_1$ = a (-1/2, 1/2 , 0)
$\mathbf{a}_2$ = a (-1/2, 0, 1/2)
$\mathbf{a}_3$ = a (0, 1/2, 1/2)

Electron density is periodic with periodicity given by $\mathbf{R}_{uvw}$

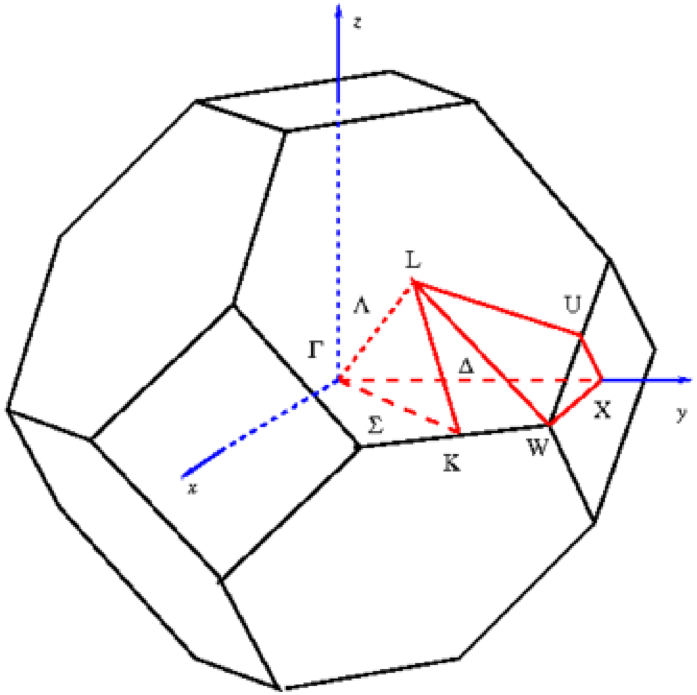
$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{R}_{uvw})$$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Electronic Bandstructure

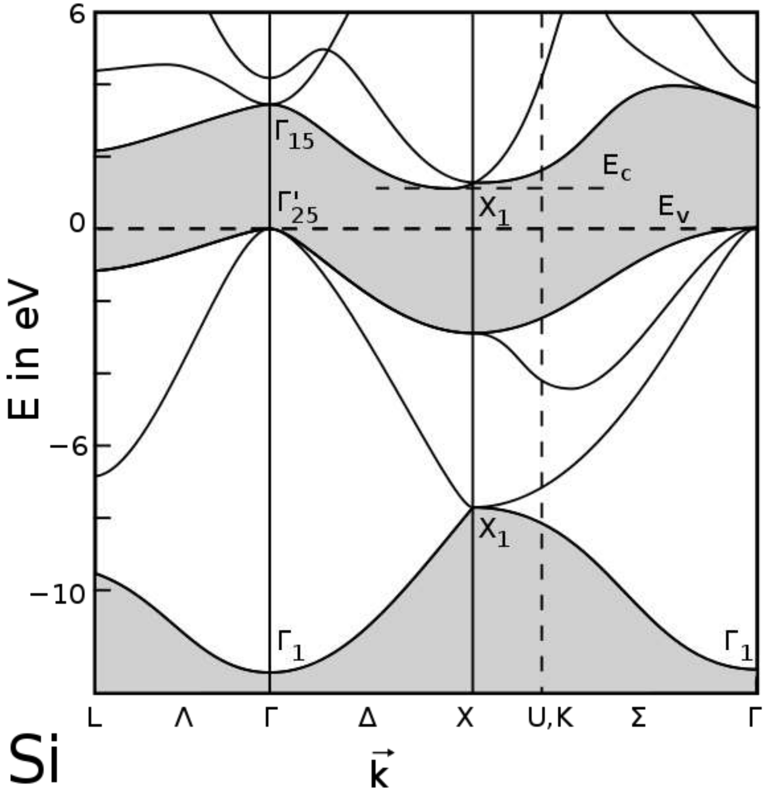
Example for Si

Brillouin Zone



http://en.wikipedia.org/wiki/Brillouin_zone

Bandstructure



http://de.wikipedia.org/wiki/Datei:Band_structure_Si_schematic.svg

Electronic wavefunctions in a crystal can be indexed by point in reciprocal space (**k**) and a band index (β)

Why?

Wavefunctions in a Crystal Obey Bloch's Theorem

For a given band β

$$f_{\mathbf{k}}^{b}(\mathbf{r}) = \exp\left(i\mathbf{k} \times \mathbf{r}\right) u_{\mathbf{k}}^{b}(\mathbf{r})$$

Where $u_{\mathbf{k}}^{b}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{b}(\mathbf{r}) = u_{\mathbf{k}}^{b}(\mathbf{r} + \mathbf{R}_{uvw})$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Representation of Electron Density

$$\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\, u_{\mathbf{k}}^{\beta}(\mathbf{r})$$

$$n(\mathbf{r}) = -e\sum_{i=1}^{N_e}\left|\phi_i(\mathbf{r})\right|^2 \longrightarrow n(\mathbf{r}) = -e\sum_{\beta}\int_{\Omega_{BZ}}\left|\phi_{\mathbf{k}}^{\beta}(\mathbf{r})\right|^2 f(\varepsilon_k^{\beta}-\varepsilon_F)\frac{d^3k}{\Omega_{BZ}}$$

Integral over k-points in first Brillouin zone

f(ε-ε_F) is Fermi-Dirac distribution function with Fermi energy ε_F

In practice the integral over the Brillouin zone is replaced with a sum over a finite number of k-points (N_{kpt})

$$n(\mathbf{r}) \approx -e\sum_{\beta}\sum_{j=1}^{N_{kpt}} w_j\left|\phi_{\mathbf{k}_j}^{\beta}(\mathbf{r})\right|^2 f(\varepsilon_{\mathbf{k}_j}^{\beta}-\varepsilon_F)$$

One parameter that needs to be checked for numerical convergence is number of k-points

Representation of Wavefunctions

Fourier-Expansion as Series of Plane Waves

For a given band: $\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\, u_{\mathbf{k}}^{\beta}(\mathbf{r})$

Recall that $u_{\mathbf{k}}^{\beta}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = u_{\mathbf{k}}^{\beta}(\mathbf{r}+\mathbf{R}_{uvw})$

$u_{\mathbf{k}}^{\beta}(\mathbf{r})$ can be written as a Fourier Series:

$$u_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{lmn} u_{\mathbf{k}}^{\beta}(\mathbf{G}_{lmn}) \exp(i\mathbf{G}_{lmn}\cdot\mathbf{r})$$

$$\mathbf{G}_{lmn} = l\mathbf{a}_1^* + m\mathbf{a}_2^* + n\mathbf{a}_3^*$$

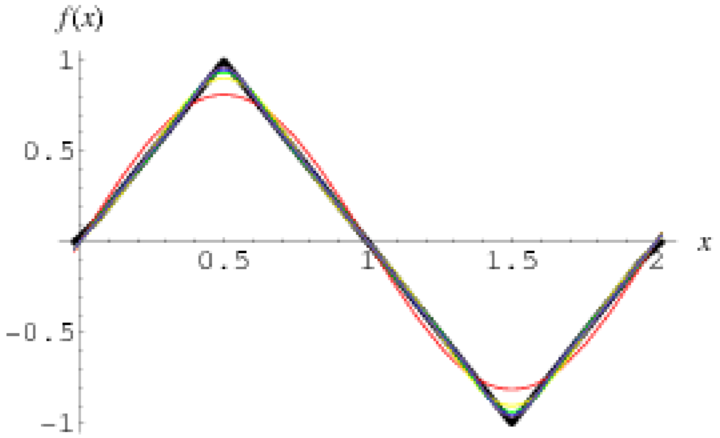
where the $\mathbf{a}_i^*$ are primitive *reciprocal lattice vectors*

$$\mathbf{a}_1^*\cdot\mathbf{a}_1 = 2\pi \qquad \mathbf{a}_1^*\cdot\mathbf{a}_2 = 0 \qquad \mathbf{a}_1^*\cdot\mathbf{a}_3 = 0$$

$$\mathbf{a}_2^*\cdot\mathbf{a}_1 = 0 \qquad \mathbf{a}_2^*\cdot\mathbf{a}_2 = 2\pi \qquad \mathbf{a}_2^*\cdot\mathbf{a}_3 = 0$$

$$\mathbf{a}_3^*\cdot\mathbf{a}_1 = 0 \qquad \mathbf{a}_3^*\cdot\mathbf{a}_2 = 0 \qquad \mathbf{a}_3^*\cdot\mathbf{a}_3 = 2\pi$$

Recall Properties of Fourier Series



Black line = (exact) triangular wave

Colored lines = Fourier series truncated at different orders

http://mathworld.wolfram.com/FourierSeriesTriangleWave.html

General Form of Fourier Series: $f(x) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx).$

For Triangular Wave: $f(x) = \frac{8}{\pi^2} \sum_{n=1,3,5,\ldots}^{\infty} \frac{(-1)^{(n-1)/2}}{n^2} \sin\left(\frac{n \pi x}{L}\right).$

Typically we expect the accuracy of a truncated Fourier series to improve as we increase the number of terms

Representation of Wavefunctions

Plane-Wave Basis Set

For a given band $\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\, u_{\mathbf{k}}^{\beta}(\mathbf{r})$

↓ *Use Fourier Expansion*

$$\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{k}}^{\beta}(\mathbf{G}) \exp\left[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}\right]$$

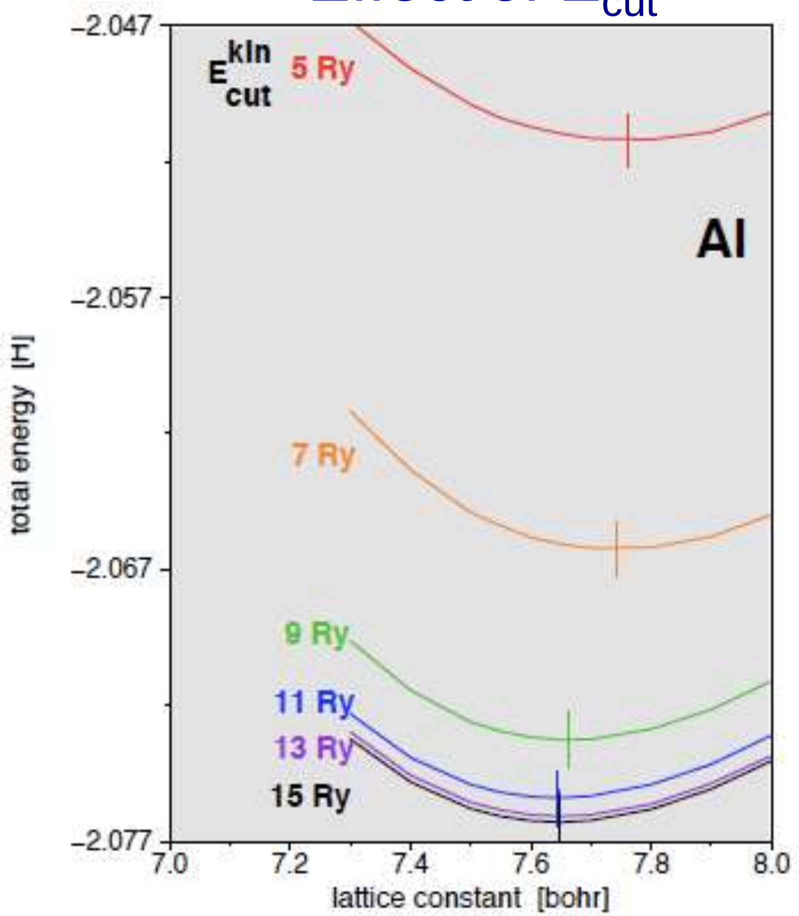
In practice the Fourier series is truncated to include all $\mathbf{G}$ for which:

$$\frac{\hbar^2}{2m}(\mathbf{G}+\mathbf{k})^2 < E_{\text{cut}}$$

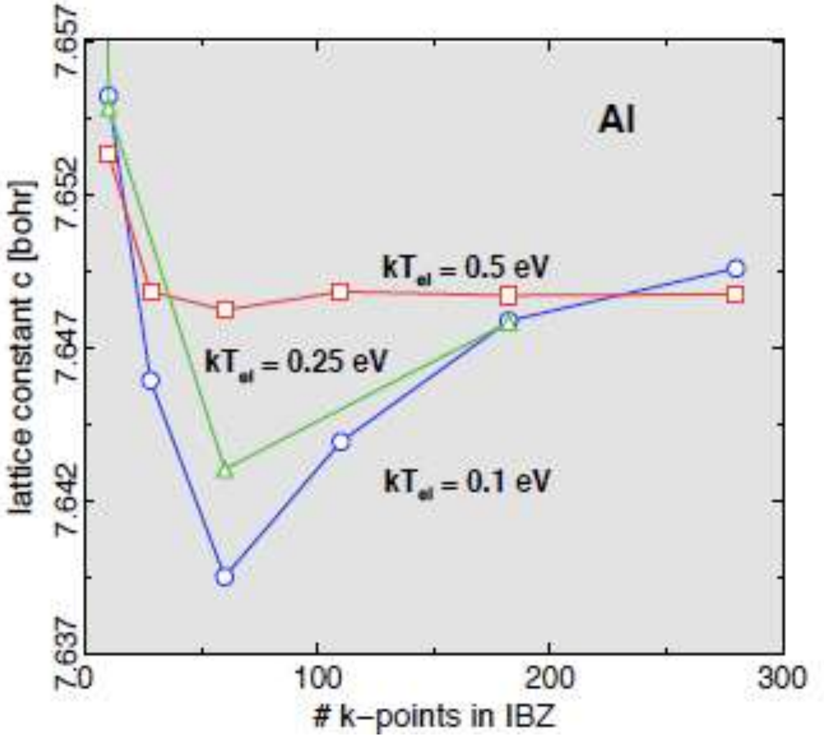
Another parameter that needs to be checked for convergence is the "plane-wave cutoff energy" E_{cut}

Examples of Convergence Checks

Effect of E_{cut}



Effect of Number of k Points



http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/pehlke1.pdf

Outline

- Formalism
  - Hydrogen Atom
  - Density Functional Theory
    - Exchange-Correlation Potentials
    - Pseudopotentials and Related Approaches
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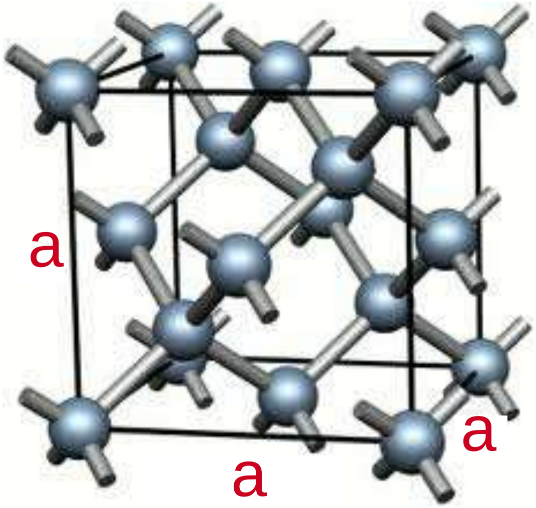
Your Exercise: Part 1

- Calculate equation of state of diamond cubic Si using Quantum Espresso on Nanohub (http://nanohub.org/)
- You will compare accuracy of LDA and GGA
- You will check numerical convergence with respect to number of k-points and plane-wave cutoff
- You will make use of the following unit cell for diamond-cubic structure



Lattice Vectors

$a_1 = a\,(-1/2,\ 1/2\ ,\ 0)$

$a_2 = a\,(-1/2,\ 0,\ 1/2)$

$a_3 = a\,(0,\ 1/2,\ 1/2)$

Basis Atom Positions

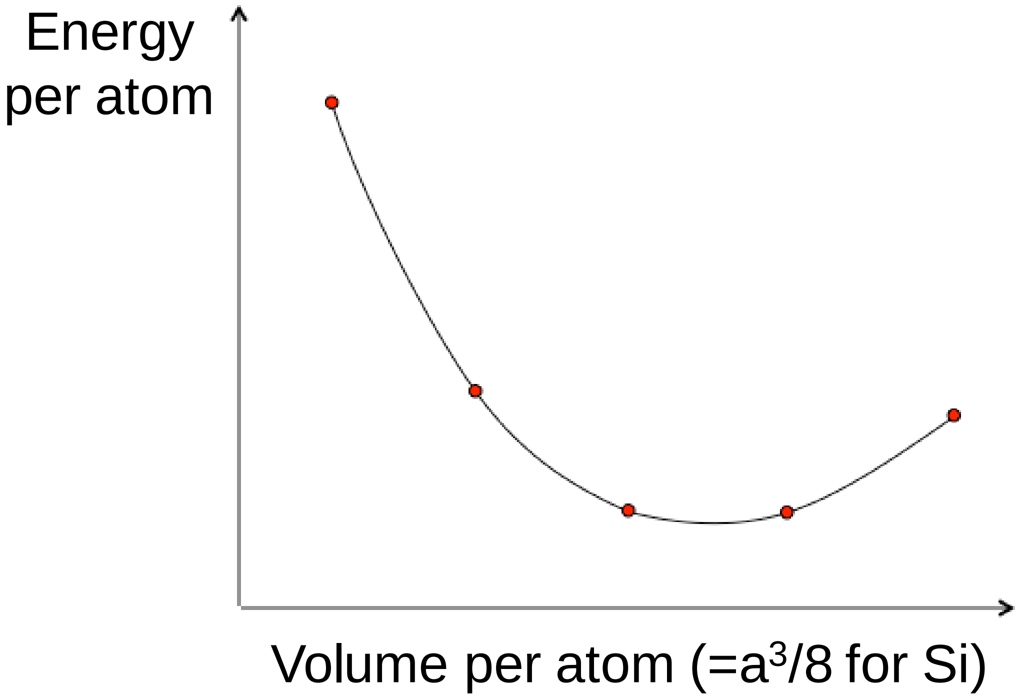
0 0 0

¼ ¼ ¼

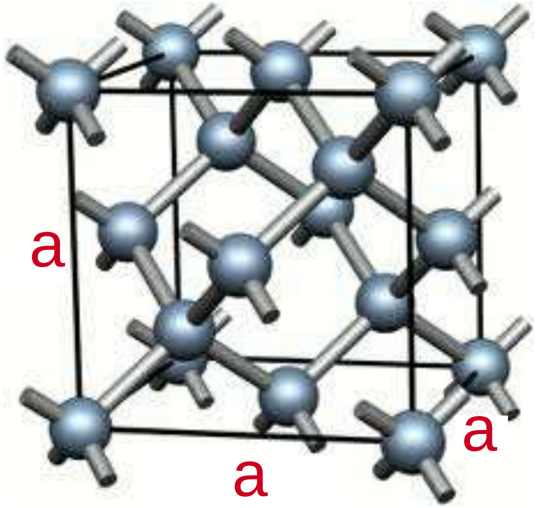
Equation of State

A Probe of Interatomic Interactions

Schematic Energy vs. Volume Relation



Diamond Cubic Structure of Si



http://www.e6cvd.com/cvd/page.jsp?pageid=361

Equation of State

What Properties Can we Learn from It?

Pressure versus Volume Relation

$$P = -\frac{\partial E}{\partial V}$$

Given *E(V)* one can compute *P(V)* by taking derivative

Recall 1st Law of Thermo: $dE = T\,dS - P\,dV$ and consider $T = 0$ K

Equilibrium Volume (or Lattice Constant)

Volume corresponding to zero pressure = Volume where slope of *E(V)* is zero
≈ Volume measured experimentally at $P = 1$ atm

Bulk Modulus

$$B = -V\frac{\partial P}{\partial V} = V\frac{\partial^2 E}{\partial V^2}$$

B related to curvature of *E(V)* Function

Your Exercise: Part 2

Non-hydrostatic Stress and Strain

Stress-Strain Relations in Linear Elasticity

$$s_{ij} = \underset{k,l}{\text{å}} C_{ijkl} e_{kl}$$

Stress

Strain

$C_{ijkl} \longrightarrow$ *Single-Crystal Elastic Constants*

Stress-Strain Relations in Linear Elasticity

Consider Single Strain $\varepsilon_{33}=\varepsilon$

$\sigma_{\square\square\square} = C_{11}\varepsilon$

$\sigma_{22\square} = C_{12}\varepsilon$

Voigt Notation (for Cubic Crystal)

$C_{3333}=C_{2222}=C_{1111}=C_{11}$

$C_{2233}=C_{1133}=C_{1122}=C_{2211}=C_{3311}=C_{3322}=C_{12}$

Lecture 8:
Introduction to Density Functional Theory

Marie Curie Tutorial Series: Modeling Biomolecules
December 6-11, 2004

Mark Tuckerman
Dept. of Chemistry
and Courant Institute of Mathematical Science
100 Washington Square East
New York University, New York, NY 10003

Background

- 1920s: Introduction of the Thomas-Fermi model.
- 1964: Hohenberg-Kohn paper proving existence of exact DF.
- 1965: Kohn-Sham scheme introduced.
- 1970s and early 80s: LDA. DFT becomes useful.
- 1985: Incorporation of DFT into molecular dynamics (Car-Parrinello) (Now one of PRL's top 10 cited papers).
- 1988: Becke and LYP functionals. DFT useful for some chemistry.
- 1998: Nobel prize awarded to Walter Kohn in chemistry for development of DFT.

Motivation

2. Electrons are quantum mechanical spin-1/2 particles and must be described by an antisymmetric wavefunction:

$$\Psi(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N)$$

3. DFT allows all properties to determined (in principle) by the electron density, $n(\mathbf{r})$, a function of just three variables, $\mathbf{r} = (x, y, z)$.

4. DFT offers an elegant formulation of N-particle quantum mechanics, conceptual simplicity, and computational efficienty.

5. Limitations of accuracy from approximation to unknown energy terms.

The many electron Hamiltonian

Consider a molecule with N nuclei at $\mathbf{R}_1, ..., \mathbf{R}_N \equiv \mathbf{R}$ and N_e electrons $(\mathbf{r}_1, ..., \mathbf{r}_{N_\mathrm{e}})$ in the Born-Oppenheimer approximation:

$$H_e = T_e + V_{ee} + V_{eN}$$

Kinetic energy:

$$T_\mathrm{e} = -\frac{1}{2}\sum_{i=1}^{N_\mathrm{e}} \nabla_i^2$$

Electron-electron repulsion:

$$V_\mathrm{ee} = \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

External Potential:

$$V_\mathrm{eN} \;=\; -\sum_{i=1}^{N_\mathrm{e}} \sum_{I=1}^{N} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \;=\; \sum_{i=1}^{N_\mathrm{e}} V_\mathrm{ext}(\mathbf{r}_i, \mathbf{R})$$

Total Molecular Hamiltonian:

$$H = H_e + T_N + V_{NN}$$

$$T_N = -\sum_{I=1}^{N} \frac{1}{2M_I} \nabla_I^2$$

$$V_{NN} = \sum_{I,J>I}^{N} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Born-Oppenheimer Approximation:

√ $$\left[T_e + V_{ee} + V_{eN}\right]\Psi(\mathrm{x}_1, \ldots, \mathrm{x}_{N_e}; \mathbf{R}) = E_0(\mathbf{R})\Psi(\mathrm{x}_1, \ldots, \mathrm{x}_{N_e}; \mathbf{R})$$

$$[T_N + V_{NN} + E_0]\chi(\mathbf{R}, t) = i\frac{\partial}{\partial t}\chi(\mathbf{R}, t)$$

$$\mathrm{x}_i = \mathbf{r}_i, s_i$$

Hohenberg-Kohn Theorem

- Two systems with the same number N_e of electrons have the same $T_e + V_{ee}$. Hence, they are distinguished only by V_{en}.

- Knowledge of |Ψ$_0$> determines V_{en}.

- Let ς be the set of external potentials such solution of

$$H_e\Psi = \left[T_e + V_{ee} + V_{eN}\right]\Psi = E_0\Psi$$

yields a non=degenerate ground state |Ψ$_0$>.

Collect all such ground state wavefunctions into a set **Ψ**. Each element of this set is associated with a Hamiltonian determined by the external potential.

There exists a 1:1 mapping C such that

$$C :\ \varsigma \longrightarrow \boldsymbol{\Psi}$$

Proof that C exists

Let V_{eN} and V'_{eN} be two elements of $\mathcal{V}$, such that

$$V_{\mathrm{eN}} \neq V'_{\mathrm{eN}} + \mathrm{const}$$

Let $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ be the associated ground state wavefunctions:

$$(T_{\mathrm{e}} + V_{\mathrm{ee}} + V_{\mathrm{eN}})|\Psi_0\rangle \quad = \quad E_0|\Psi_0\rangle \qquad (1)$$

$$\left(T_e + V_{ee} + V'_{eN}\right)\left|\Psi'_0\right\rangle \; = \; E'_0\left|\Psi'_0\right\rangle \qquad (2)$$

We will show that $|\Psi_0\rangle = |\Psi'_0\rangle$ leads to a contradiction.

Subtract (2) from (1):

$$(V_{\mathrm{eN}} - V'_{\mathrm{eN}})|\Psi_0\rangle = (E_0 - E'_0)|\Psi_0\rangle$$

Since V_{eN} and V'_{eN} are multiplicative operators:

$$V_{\mathrm{eN}} - V'_{\mathrm{eN}} = E_0 - E'_0$$

thus *contradicting* the original assumption.

Inverse Map:

$$\mathrm{C}^{-1} : \mathbf{\Psi} \longrightarrow \mathcal{V}$$

$$|\Psi_0\rangle \neq |\Psi_0'\rangle \Rightarrow V_{\mathrm{eN}} \neq V_{\mathrm{eN}}'$$

Assume $V_{\mathrm{eN}} = V_{\mathrm{eN}}'$, **then**:

$$(T_{\mathrm{e}} + V_{\mathrm{ee}} + V_{\mathrm{eN}})\,|\Psi_0\rangle \;=\; E_0|\Psi_0\rangle$$

$$\left(T_e + V_{ee} + V_{eN}\right)\left|\Psi_0'\right\rangle = E_0'\left|\Psi_0'\right\rangle$$

$|\Psi_0'\rangle$ cannot be a ground state of H_{e}. But it must be a ground state of $H_{\mathrm{e}}' = H_{\mathrm{e}}$, which is a contradiction.

Hohenberg-Kohn Theorem (part II)

Given an antisymmetric ground state wavefunction from the set **Ψ**, the ground-state density is given by

$$n(\mathbf{r}) = N_e \sum_{s_1} \cdots \sum_{s_{N_e}} \int d\mathbf{r}_2 \cdots d\mathbf{r}_{N_e} \left| \Psi(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{N_e}, s_{N_e}) \right|^2$$

Knowledge of $n(\mathbf{r})$ is sufficient to determine |Ψ>

Let N be the set of ground state densities obtained from N_e-electron ground state wavefunctions in **Ψ.** Then, there exists a 1:1 mapping

$$D : \mathbf{\Psi} \longrightarrow \mathrm{N} \qquad\qquad D^{-1} : \mathrm{N} \longrightarrow \mathbf{\Psi}$$

The formula for $n(\mathbf{r})$ shows that D exists, however, showing that D^{-1} exists Is less trivial.

Proof that D^{-1} exists

Ground state expectation values:

$$E_0 = \langle \Psi_0 | H_\mathrm{e} | \Psi_0 \rangle = \langle \Psi_0 | T_\mathrm{e} + V_\mathrm{ee} + V_\mathrm{eN} | \Psi_0 \rangle$$

$$E_0' = \langle \Psi_0' | H_e' | \Psi_0' \rangle = \langle \Psi_0' | T_e + V_{ee} + V_{eN}' | \Psi_0' \rangle$$

By the Ritz principle:

$$E_0 < \langle \Psi_0' | H_\mathrm{e} | \Psi_0' \rangle$$

However

$$\begin{aligned} \langle \Psi_0' | H_\mathrm{e} | \Psi_0' \rangle &= \langle \Psi_0' | H_\mathrm{e}' + V_\mathrm{eN} - V_\mathrm{eN}' | \Psi_0' \rangle \\ &= E_0' + \langle \Psi_0' | V_\mathrm{eN} - V_\mathrm{eN}' | \Psi_0' \rangle \end{aligned}$$

Note:

$$\begin{aligned}
\langle \Psi_0 | V_{\mathrm{eN}} | \Psi_0 \rangle &= \int d\mathbf{x}_1 \cdots d\mathbf{x}_{N_\mathrm{e}} \sum_{i=1}^{N_\mathrm{e}} V_{\mathrm{ext}}(\mathbf{r}_i) |\Psi_0(\mathbf{x}_1, ..., \mathbf{x}_{N_\mathrm{e}})|^2 \\
&= \sum_{i=1}^{N_\mathrm{e}} \int d\mathbf{x}_1 \cdots d\mathbf{x}_{N_\mathrm{e}} V_{\mathrm{ext}}(\mathbf{r}_i) |\Psi_0(\mathbf{x}_1, ..., \mathbf{x}_{N_\mathrm{e}})|^2 \\
&= N_\mathrm{e} \int d\mathbf{r}\; V_{\mathrm{ext}}(\mathbf{r}) \sum_s \int d\mathbf{x}_2 \cdots d\mathbf{x}_{N_\mathrm{e}} |\Psi_0(\mathbf{r}, s, ..., \mathbf{x}_{N_\mathrm{e}})|^2 \\
&= \int d\mathbf{r}\; V_{\mathrm{ext}}(\mathbf{r}) n_0(\mathbf{r})
\end{aligned}$$

Starting instead with

$$E_0' < \langle \Psi_0 | H_e' | \Psi_0 \rangle$$

one can show that

$$E_0' < E_0 - \int d\mathbf{r}\; n_0(\mathbf{r})\,[V_{\rm ext}(\mathbf{r}) - V_{\rm ext}'(\mathbf{r})]$$

Composite Map

The maps C^{-1} and D^{-1} exist, hence

$$(CD)^{-1}\ :\ \mathrm{N} \longrightarrow \varsigma$$

is a 1:1 map that maps ground state densities uniquely to external potentials.

- Knowledge of $n_0(\mathbf{r})$ determines V_{eN} and, thus, H_{e}.
- $n_0(\mathbf{r})$ determines all of the properties of a system.
- Given an operator $\hat{O}$, the expectation value:

$$\boxed{\left\langle \Psi_0[n_0] \middle| \hat{O} \middle| \Psi_0[n_0] \right\rangle = O[n_0]}$$

is a *unique functional* of $n_0(\mathbf{r})$

The theorems are generalizable to degenerate ground states!

The energy functional

The energy expectation value is of particular importance

$$\left\langle \Psi_0[n_0] \middle| H_e \middle| \Psi_0[n_0] \right\rangle = E[n_0]$$

From the variational principle, for |Ψ> in **Ψ**:

$$\left\langle \Psi \middle| H_e \middle| \Psi \right\rangle \geq \left\langle \Psi_0 \middle| H_e \middle| \Psi_0 \right\rangle$$

Thus,

$$\left\langle \Psi[n] \middle| H_e \middle| \Psi[n] \right\rangle = E[n] \geq E[n_0]$$

Therefore, $E[n_0]$ can be determined by a minimization procedure:

$$E[n_0] = \min_{n(\mathbf{r}) \in \mathrm{N}} E[n]$$

Hohenberg-Kohn Functional

Two systems with N_e electrons are distinguished *only* by the external potential. Therefore,

$$
\begin{aligned}
E[n] &= \langle \Psi | T_e + V_{ee} | \Psi \rangle + \int d\mathbf{r}\, n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}, \mathbf{R}) \\
&= T_e[n] + V_{ee}[n] + \int d\mathbf{r}\, n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}, \mathbf{R}) \\
&= F[n] + \int d\mathbf{r}\, n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}, \mathbf{R})
\end{aligned}
$$

The functional $F[n]$ is the same for *all* N_e-electron systems.

$F[n]$ is, therefore, a *universal* functional known as the Hohenberg-Kohn functional.

Hohenberg-Kohn Minimization

Minimize $E[n]$ subject to the condition:

$$\int d\mathbf{r}\; n(\mathbf{r}) = N_{\mathrm{e}}$$

Minimization Procedure:

$$\frac{\delta}{\delta n(\mathbf{r})}\left[E[n] - \mu\left(\int d\mathbf{r}\; n(\mathbf{r}) - N_{\mathrm{e}}\right)\right] = 0$$

μ is a *Lagrange Multiplier* related to the chemical potential.

Hohenberg-Kohn equation:

$$\frac{\delta F}{\delta n(\mathbf{r})} + V_{\mathrm{ext}}(\mathbf{r}, \mathbf{R}) = \mu$$

where use has been made of the identity:

$$\frac{\delta}{\delta n(\mathbf{r})}\int d\mathbf{r}'\; f(n(\mathbf{r}')) = \int d\mathbf{r}'\; \frac{\partial f}{\partial n(\mathbf{r}')}\delta(\mathbf{r}-\mathbf{r}') = \frac{\partial f}{\partial n(\mathbf{r})}$$

v-representability

A density $n(\mathbf{r})$ is $v-representable$ if is associated with an antisymmetric ground state wavefunction of $some$ Hamiltonian H_e distinguished by $a\ particular$ external potential $V_\mathrm{ext}(\mathbf{r},\mathbf{R})$.

- Not all densities are v-representable.
- There is no general way to tell if a density is v-representable.
- Since Hohenberg-Kohn theorem maps v-representable densities to ground state wavefunctions, the minimization must be carried out over v-representable densities.

N-representability

A density $n(\mathbf{r})$ is *$N-$representable* if it is associated with an antisymmetric wavefunction, not necessarily a ground state wavefunction associated with a Hamiltonian H_e.

Requires:

$$n(\mathbf{r}) \geq 0 \qquad \int d\mathbf{r}\; n(\mathbf{r}) = N_\mathrm{e}$$

- Given $|\Psi\rangle$, easily determine $n(\mathbf{r})$.
- Given $n(\mathbf{r})$, cannot easily determine $|\Psi\rangle$.
- Particularly, given $n_0(\mathbf{r})$, how can we tell if it came from $|\Psi_0\rangle$ or some other $|\Psi_{n_0}\rangle$.

Levy constrained search

Hohenberg-Kohn functional satisfies

$$F[n_0] = \min_{|\psi_{n_0}\rangle \to n_0} \langle \Psi_{n_0} | T_\mathrm{e} + V_\mathrm{ee} | \psi_{n_0} \rangle$$

Define:

$$\tilde{F}[n] = \min_{|\Psi\rangle \to n(\mathbf{r})} \langle \Psi | T_\mathrm{e} + V_\mathrm{ee} | \Psi \rangle$$

Since $\tilde{F}[n_0] = F[n_0]$, we can reformulate Hohenberg-Kohn minimization as:

$$\begin{aligned} E_0 &= \min_{n(\mathbf{r}) \in \mathcal{N}} \left[\min_{|\Psi\rangle \to n(\mathbf{r})} \langle \Psi | T_\mathrm{e} + V_\mathrm{ee} | \Psi \rangle + \int d\mathbf{r}\; n(\mathbf{r}) V_\mathrm{ext}(\mathbf{r}) \right] \\ &= \min_{n(\mathbf{r})} \left[F[n] + \int d\mathbf{r}\; n(\mathbf{r}) V_{ext}(\mathbf{r}) \right] \end{aligned}$$

which only requires N-representable densities.

Thomas-Fermi Theory

Ideal Fermi Gas of constant density n:

$$\psi_{\mathbf{n}}(\mathbf{r}) = \frac{1}{L^{3/2}} e^{2\pi i \mathbf{n}\cdot\mathbf{r}}$$

$$\varepsilon_{\mathbf{n}} = \frac{2\pi^2}{L^2}\mathbf{n}^2$$

$$f_{\mathbf{n}} = \begin{cases} 1 & \varepsilon_{\mathbf{n}} < \varepsilon_F \\ 0 & \varepsilon_{\mathbf{n}} > \varepsilon_F \end{cases}$$

Kinetic energy per particle:

$$t = \sum_{\mathbf{n}} f_{\mathbf{n}} \varepsilon_{\mathbf{n}} = C_F n^{5/3}$$

Local density approximation: $n \longrightarrow n(\mathbf{r})$

$$T_{\mathrm{e}}[n] = C_F \int d\mathbf{r}\; n^{5/3}(\mathbf{r})$$

Exchange energy:

- **One-particle density matrix:**

$$\rho(\mathbf{r},\mathbf{r}') = N_e \sum_{\{s\}} \int d\mathbf{r}_2 \cdots d\mathbf{r}_{N_e} \Psi^*(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{N_e}, s_{N_e}) \Psi(\mathbf{r}', s_1, \mathbf{r}_2, s_2, \ldots, \mathbf{r}_{N_e}, s_{N_e})$$

- **Exchange energy density:**

$$k = -\frac{1}{4V} \int d\mathbf{r}\, d\mathbf{r}' \frac{|\rho(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} = -C_x n^{4/3}$$

- **Local density approximation:**

$$E_x[n] = -C_x \int d\mathbf{r}\; n^{4/3}(\mathbf{r})$$

Approximate energy functional:

$$\begin{aligned} E[n] &= C_F \int d\mathbf{r}\; n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\; \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &- C_x \int d\mathbf{r}\; n^{4/3}(\mathbf{r}) + \int d\mathbf{r}\; n(\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r},\mathbf{R}) \end{aligned}$$

The Kohn-Sham Formulation

Central assertion of KS formulation: Consider a system of N_e Non-interacting electrons subject to an "external" potential V_{KS}. It Is possible to choose this potential such that the ground state density Of the non-interacting system is the same as that of an interacting System subject to a particular external potential V_{ext}.

A non-interacting system is separable and, therefore, described by a set of single-particle orbitals $\psi_i(\mathbf{r},\mathrm{s})$, $\mathrm{i}=1,\ldots,N_e$, such that the wave function is given by a Slater determinant:

$$\Psi(\mathrm{x}_1,\ldots,\mathrm{x}_{N_e}) = \frac{1}{\sqrt{N_e!}}\det[\psi_1(\mathrm{x}_1)\cdots\psi_{N_e}(\mathrm{x}_{N_e})]$$

The density is given by

$$n(\mathbf{r}) = \sum_{i=1}^{N_e}\sum_s |\psi_i(\mathrm{x})|^2 \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij}$$

The kinetic energy is given by

$$T_s = -\frac{1}{2}\sum_{i=1}^{N_e}\sum_s\int d\mathbf{r}\ \psi_i^*(\mathrm{x})\nabla^2\psi_i(\mathrm{x})$$

Kohn-Sham Equations

The variational problem can now be formulated as:

$$\frac{\delta}{\delta\psi_i^*(\mathbf{x})}\left[-\frac{1}{2}\sum_j\int d\mathbf{x}\psi_j^*(\mathbf{x})\nabla^2\psi_j(\mathbf{x})+\int d\mathbf{x}\; V_{\mathrm{KS}}(\mathbf{r})n(\mathbf{r})\right.$$
$$\left.-\sum_{j,k}\lambda_{jk}\left(\int d\mathbf{x}\psi_j^*(\mathbf{x})\psi_k(\mathbf{x})-\delta_{ij}\right)\right]=0$$

The Kohn-Sham Potential

Kohn-Sham functional:

$$\begin{aligned} E_{\mathrm{KS}}[n] &= T_{\mathrm{nonint}}[\{\psi\}] + \int d\mathbf{r} V_{\mathrm{KS}}(\mathbf{r}) n(\mathbf{r}) \\ &= T_{\mathrm{nonint}}[\{\psi\}] + \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &+ E_{\mathrm{xc}}[n] + \int d\mathbf{r} V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

where, in principle,

$$E_{\mathrm{xc}}[n] = F[n] - \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - T_{\mathrm{nonint}}[n]$$

is called the *exchange-correlation* energy functional. Its exact form is not known, so approximations are necessary.

$$V_{\mathrm{KS}} = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \;\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

Closed shell systems

Suppose there is an even number of electrons, so that they all can be paired up and the external potential $V_{\text{ext}}(\mathbf{r})$ is independent of spin. Spin-up and spin-down contribute equally to the total density:

$$n^{(\uparrow)}(\mathbf{r}) = n^{(\downarrow)}(\mathbf{r}) = \frac{1}{2}n(\mathbf{r})$$

Therefore, we only need $N_{\text{e}}/2$ Kohn-Sham orbitals, to each of which we assign an *occupation number* of $f = 2$. These orbitals satisfy the orthogonality condition:

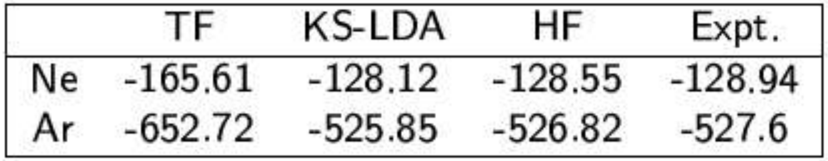
$$\int d\mathbf{r}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = f\delta_{ij}$$

The density and kinetic energy are then given by

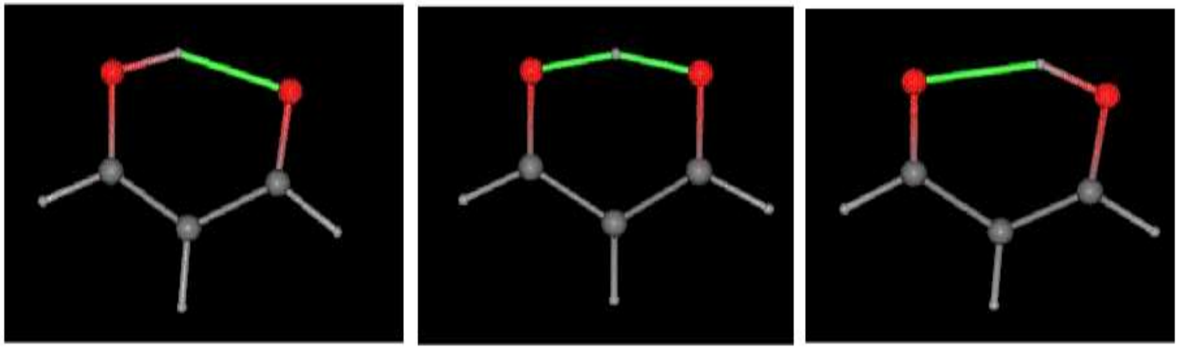
$$n(\mathbf{r}) = \sum_{i=1}^{N_{\text{e}}/2} |\psi_i(\mathbf{r})|^2$$

$$T_s = -\frac{1}{2}\sum_{i=1}^{N_e/2} \left\langle \psi_i(\mathbf{r}) \right| \nabla^2 \left| \psi_i(\mathbf{r}) \right\rangle$$

Some simple results from DFT



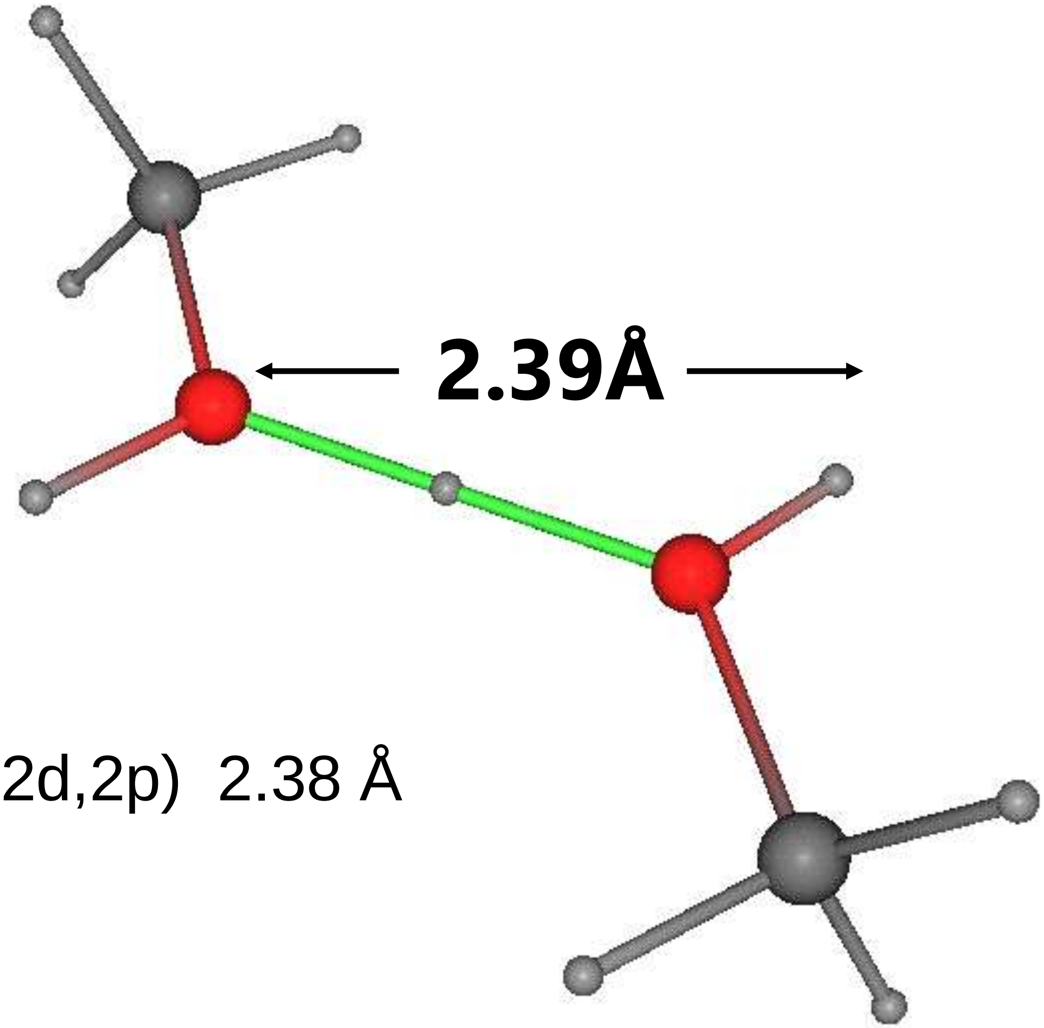
	TF	KS-LDA	HF	Expt.
Ne	-165.61	-128.12	-128.55	-128.94
Ar	-652.72	-525.85	-526.82	-527.6



E_{barrier}(DFT) = 3.6 kcal/mol

E_{barrier}(MP4) = 4.1 kcal/mol

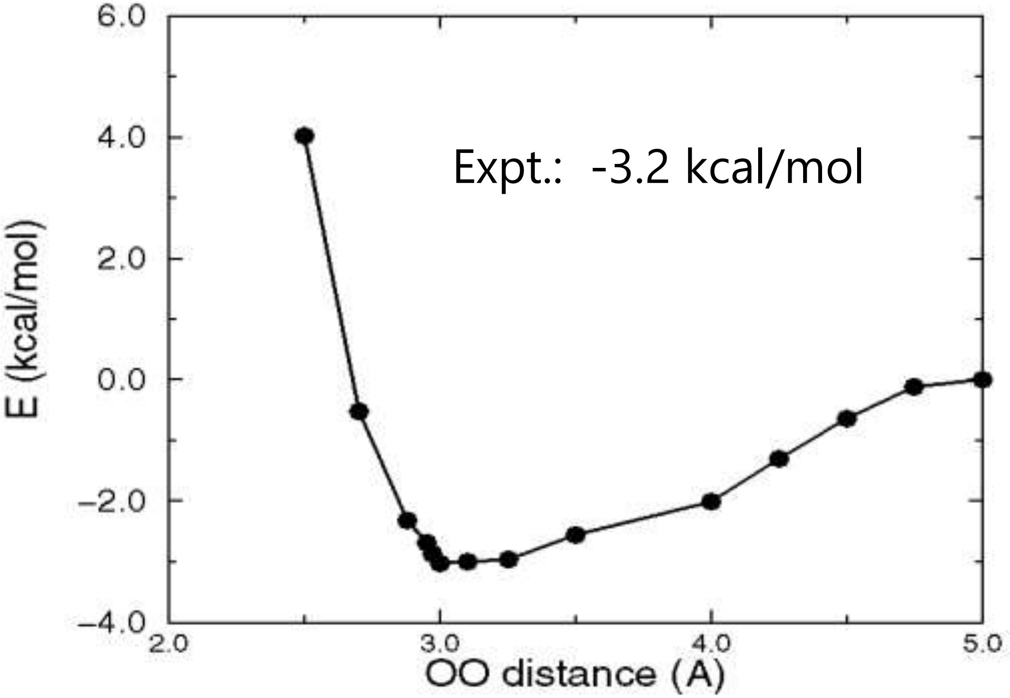
Geometry of the protonated methanol dimer



MP2 6-311G (2d,2p) 2.38 Å

Results methanol

Dimer dissociation curve of a *neutral* dimer



Expt.: -3.2 kcal/mol

Lecture Summary

- Density functional theory is an exact reformulation of many-body quantum mechanics in terms of the probability density rather than the wave function

- The ground-state energy can be obtained by minimization of the energy functional E[n]. All we know about the functional is that it exists, however, its form is unknown.

- Kohn-Sham reformulation in terms of single-particle orbitals helps in the development of approximations and is the form used in current density functional calculations today.

experimental methods

Get a diamond anvil cell

Get beamtime on a synchrotron

Load your cell.
Put medium.

Go to synchrotron

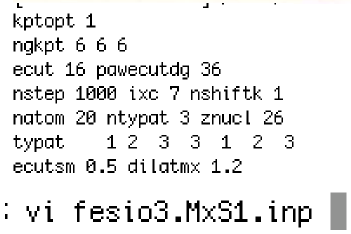
Run your experiment

computational methods

abinit.org

Get an ab initio software package

Get time on a supercomputer



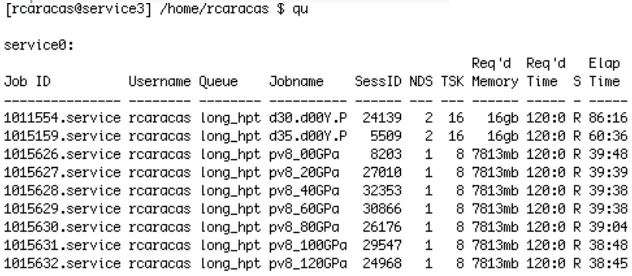
```
kptopt 1
ngkpt 6 6 6
ecut 16 pawecutdg 36
nstep 1000 ixc 7 nshiftk 1
natom 20 ntypat 3 znucl 26
typat    1 2  3  3  1  2  3
ecutsm 0.5 dilatmx 1.2

: vi fesio3.MxS1.inp
```

Input your structure.
Choose pseudos, XCs.

User Name: rcaracas

Password: ••••••••

Go to supercomputer



```
[rcaracas@service3] /home/rcaracas $ qu

service0:
                                                                   Req'd  Req'd   Elap
Job ID          Username Queue    Jobname    SessID NDS TSK Memory Time  S Time
--------------- -------- -------- ---------- ------ --- --- ------ ----- - -----
1011554.service rcaracas long_hpt d30.d00Y.P  24139   2  16   16gb 120:0 R 86:16
1015159.service rcaracas long_hpt d35.d00Y.P   5509   2  16   16gb 120:0 R 60:36
1015626.service rcaracas long_hpt pv8_00GPa    8203   1   8 7813mb 120:0 R 39:48
1015627.service rcaracas long_hpt pv8_20GPa   27010   1   8 7813mb 120:0 R 39:39
1015628.service rcaracas long_hpt pv8_40GPa   32353   1   8 7813mb 120:0 R 39:38
1015629.service rcaracas long_hpt pv8_60GPa   30866   1   8 7813mb 120:0 R 39:38
1015630.service rcaracas long_hpt pv8_80GPa   26176   1   8 7813mb 120:0 R 39:04
1015631.service rcaracas long_hpt pv8_100GPa  29547   1   8 7813mb 120:0 R 38:48
1015632.service rcaracas long_hpt pv8_120GPa  24968   1   8 7813mb 120:0 R 38:45
```

Run your experiment

What is it hard to calculate ?

Transport properties: thermal conductivity, electrical conductivity of insulators, rheology, diffusion

Excited electronic states: optical spectra ☹ (=constants?)

Width of IR/Raman peaks, **Melting curves**, **Fluid properties**

What we can calculate ?

Electronic properties: orbital energies, chemical bonding, electrical conductivity

Structural properties: prediction of structures (under extreme conditions), phase diagrams, surfaces, interfaces, amorphous solids

Mechanical properties: elasticity, compressibility, thermal expansion

Dielectric properties: hybridizations, atomic dynamic charges, dielectric susceptibilities, polarization, non-linear optical coefficients, piezoelectric tensor

Spectroscopic properties: Raman spectra with peak position and intensity, IR peaks

Dynamical properties: phonons, lattice instabilities, prediction of structures, thermodynamic properties, phase diagrams, thermal expansion

A set of N particles with masses m_n and initial positions X_n

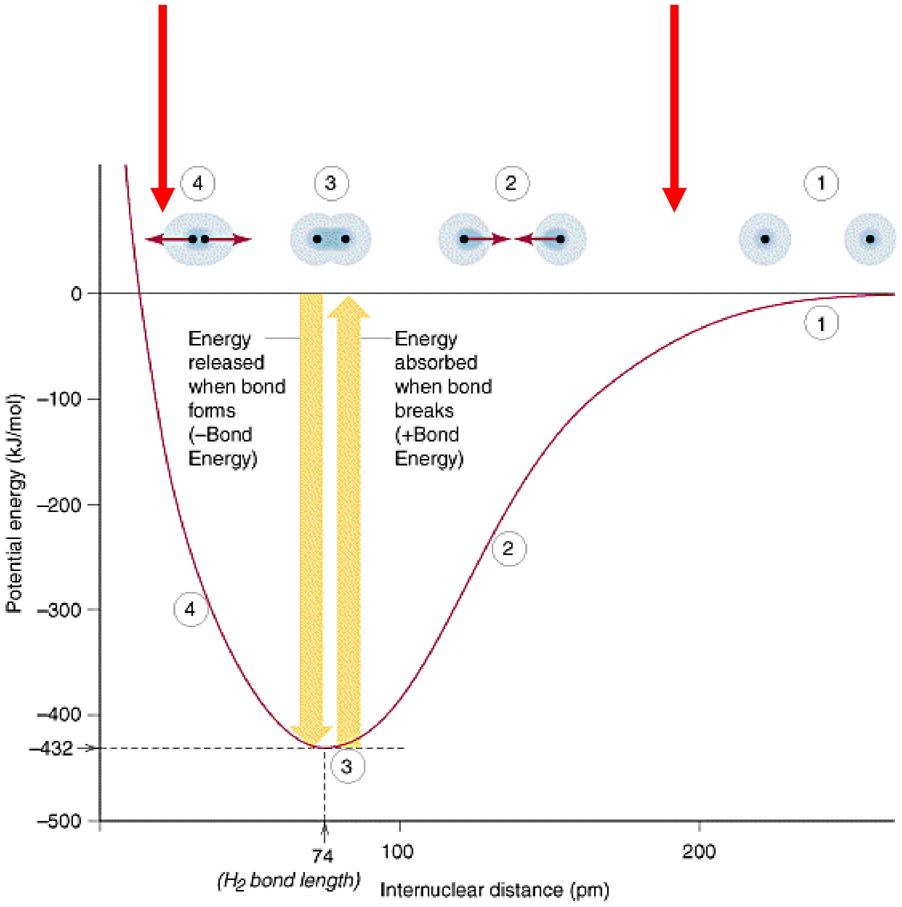
t: $\mathbf{X_t}$ $\dot{\mathbf{X}}_{\mathbf{t}}$ (=V) $\ddot{\mathbf{X}}_{\mathbf{t}}$(=A) $\mathbf{m}$

Compute new F
then F = ma

t+1: $\mathbf{X_{t+1}}$ $\dot{\mathbf{X}}_{\mathbf{t+1}}$ $\ddot{\mathbf{X}}_{\mathbf{t+1}}$ $\mathbf{m}$

Repulsive zone

Attractive zone



Two-body potentials *or* pair potentials

Lennard-Jones

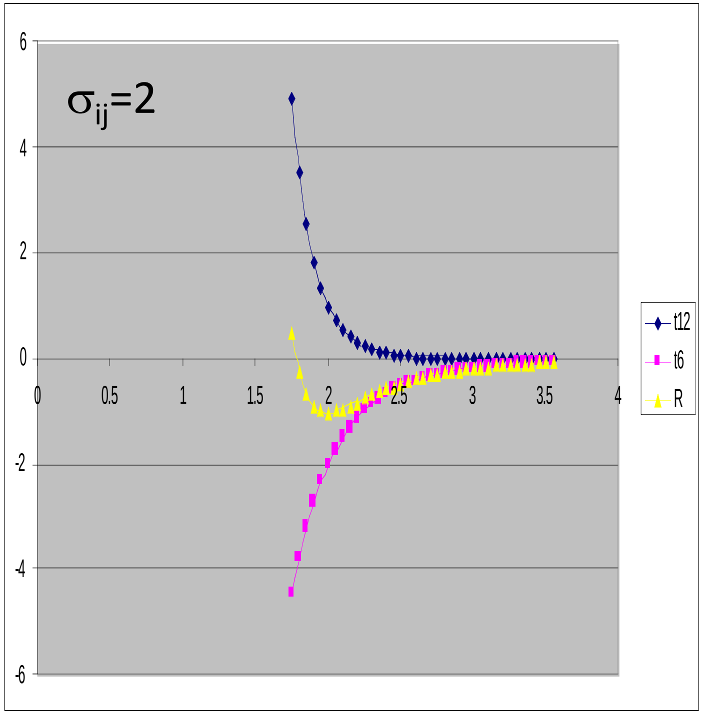
$$V(r_{ij}) = \epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

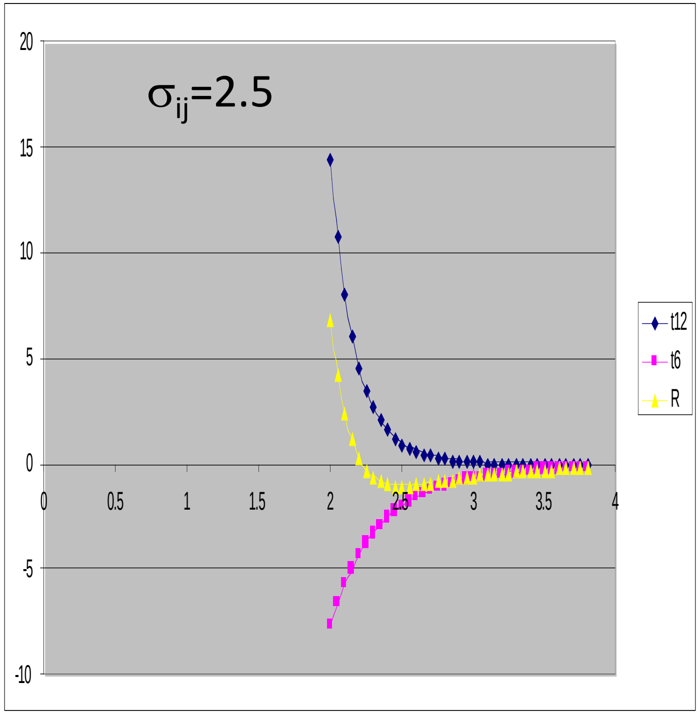
Morse

$$V(r_{ij}) = \epsilon_{ij}\left[\left(1 - \mathrm{e}^{-\alpha_{ij}(r_{ij}-\sigma_{ij})}\right)^{2} - 1\right]$$

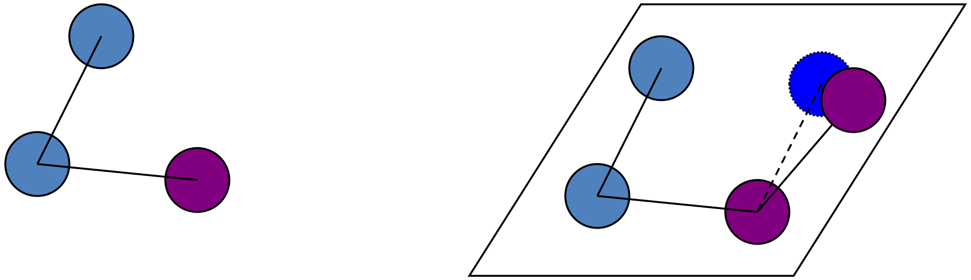
Buckingham

$$V(r_{ij}) = A_{ij}\exp\left(-\frac{r_{ij}}{\sigma_{ij}}\right) - C_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}$$





Multibody potentials

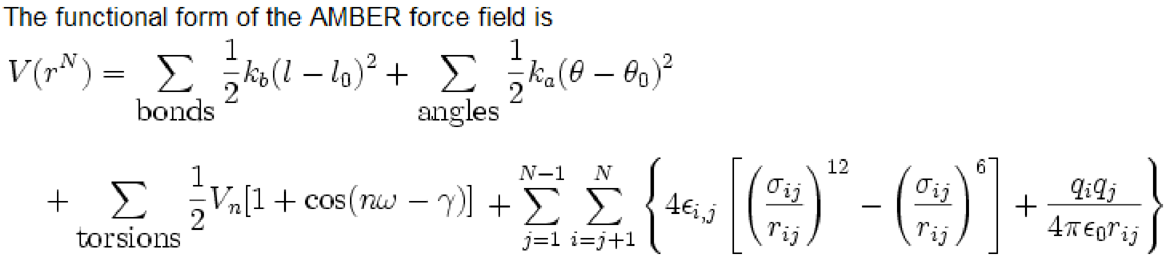


$$V_{ij}(r_{ij}) = V_{repulsive}(r_{ij}) + b_{ijk}V_{attractive}(r_{ij})$$

2 body

3+ body

Force fields – very good for molecules



The functional form of the AMBER force field is

$$V(r^N) = \sum_{\text{bonds}} \frac{1}{2} k_b (l - l_0)^2 + \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2$$

$$+ \sum_{\text{torsions}} \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)] + \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \left\{ 4\epsilon_{i,j} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

Many other examples:
CHARMM, polarizable, valence-bond models,

Tersoff interatomic potential

$$E = \sum_i V_1(r_i) + \sum_{i<j} V_2(r_i, r_j) + \sum_{i<j<k} V_3(r_i, r_j, r_k) + \ldots$$

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

$$f_R(r) = Ae^{(-\lambda_1 r)}$$

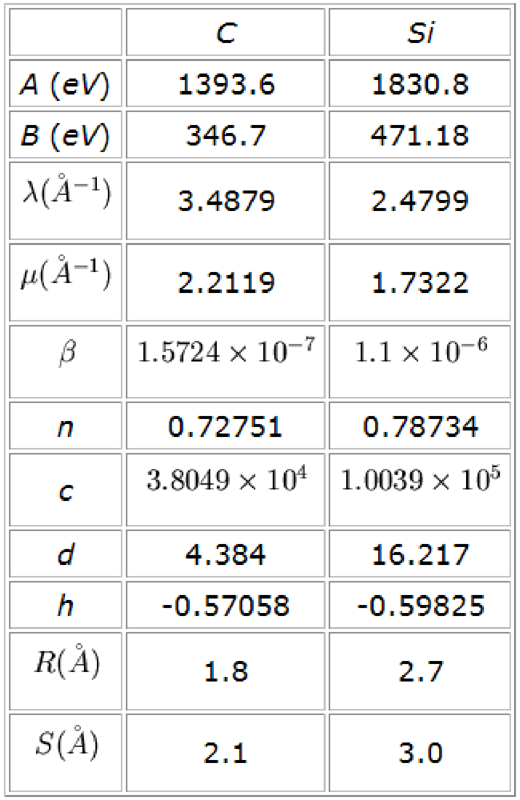
$$f_C(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin[\frac{\pi}{2}(r-R)/D], & R - D < r < R + D \\ 0, & r > R + D \end{cases}$$

$$b_{ij} = \frac{1}{(1 + \beta^n \zeta_{ij}^n)^{1/2n}}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ij}) g(\theta_{ijk}) e^{[\lambda_3^3 (r\mathrm{ij} - r\mathrm{ik})^3]}$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos\theta)^2]}$$

Table 7.1: Parameters for the Tersoff potential, for atoms of carbon and silicon.



	C	*Si*
A (*eV*)	1393.6	1830.8
B (*eV*)	346.7	471.18
$\lambda(\mathring{A}^{-1})$	3.4879	2.4799
$\mu(\mathring{A}^{-1})$	2.2119	1.7322
β	1.5724×10^{-7}	1.1×10^{-6}
n	0.72751	0.78734
c	3.8049×10^4	1.0039×10^5
d	4.384	16.217
h	-0.57058	-0.59825
$R(\mathring{A})$	1.8	2.7
$S(\mathring{A})$	2.1	3.0

http://phycomp.technion.ac.il/~david/thesis/these2.html

Non-empirical = first-principles or *ab initio*

- the energy is *exactly* calculated
- no experimental input

\+ transferability, accuracy, many properties

\- small systems

Schrödinger equation

time-dependent

$$H(t)\,|\psi_n(t)> = i\hbar\frac{\partial}{\partial t}|\psi_n(t)>$$

time-independent

$$[-\frac{\hbar^2}{2m}\nabla^2 + U(r)\,|\psi_n> = E_n\,|\psi_n>$$

E_n Eigenvalues

$|\psi_n>$ Eigenstates

$$H\Psi = [T+V+U]\,\Psi = \left[\sum_{i}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i}^{N} V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i,\vec{r}_j)\right]\Psi = E\Psi$$

Kinetic energy of the electrons

External potential

Schrödinger equation involves many-body interactions

Wavefunction

$|y_n>$ -contains all the measurable information
-gives a measure of probability: $<y_n|y_n>=y^*y$

$|y_n>$ ~ many-particle wavefunction:
depends on the position of electrons and nuclei
scales factorial

For a system like C atom: 6 electrons : 6! evaluations = 720

For a system like O atom: 8 electrons : 8! evaluations = 40320

For a system like Ne atom: 10 electrons: 10! Evaluations = 3628800

For one SiO_2 molecule: 30electrons+3nuclei= $8.68E^{36}$ evaluations

UNPRACTICAL!

DENSITY FUNCTIONAL THEORY

- What is DFT ?
- Codes
- Planewaves and pseudopotentials
- Types of calculation
- Input key parameters
- Standard output
- Examples of properties:
    - Electronic band structure
    - Equation of state
    - Elastic constants
    - Atomic charges
    - Raman and Infrared spectra
    - Lattice dynamics and thermodynamics

THEORETICAL ASPECTS

PRACTICAL ASPECTS

EXAMPLES

What is DFT

Idea:
one determines the ***electron density*** (Kohn, Sham in the sixties: the one responsible for the chemical bonds) from which by proper integrations and derivations all the other properties are obtained.

INPUT

Structure: atomic types + atomic positions =
initial guess of the geometry

There is no experimental input !

What is DFT

$$E[n(r)] = T_s[n(r)] + E_{ext}[n(r)] + E_{col}[n(r)] + E_{xc}[n(r)]$$

Kinetic energy of non-interacting electrons

Energy term due to exterior

Coulombian energy = $E_{ee} + E_{eN} + E_{NN}$

Exchange correlation energy

Electron spin:

Decrease energy

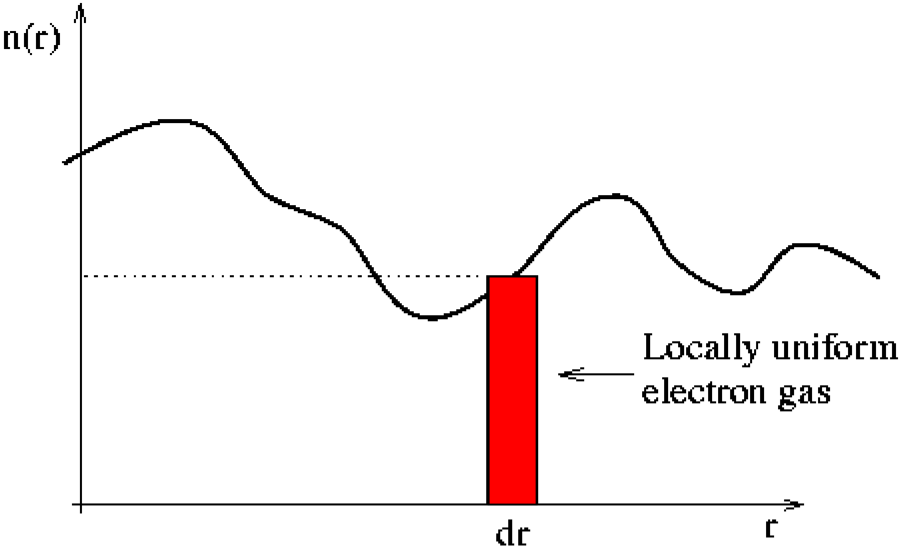
Increases

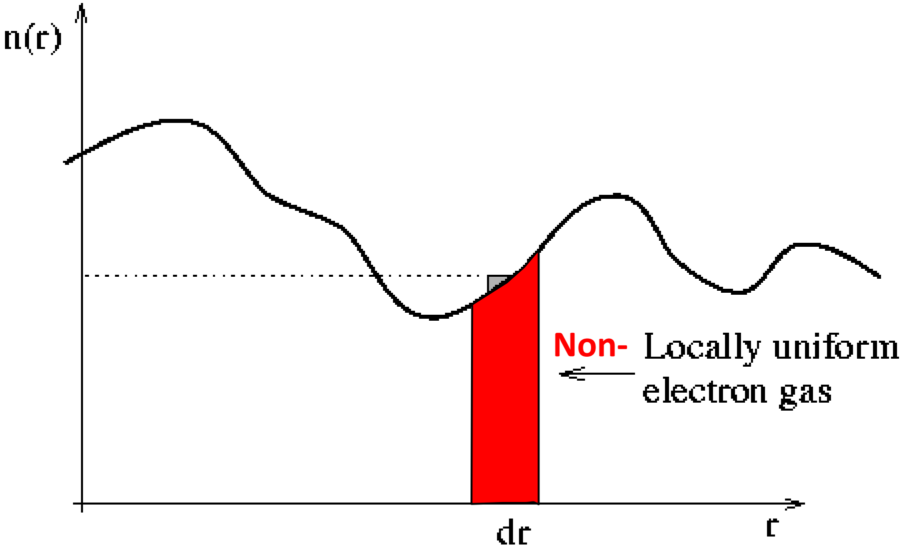
$$n(r) = N\int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \psi^*(r, r_2, r_3, \ldots., r_N)\psi(r, r_2, r_3, \ldots, r_N)$$

E_{xc}: LDA vs. GGA

LDA = Local Density Approximation

GGA = Generalized Gradient Approximation

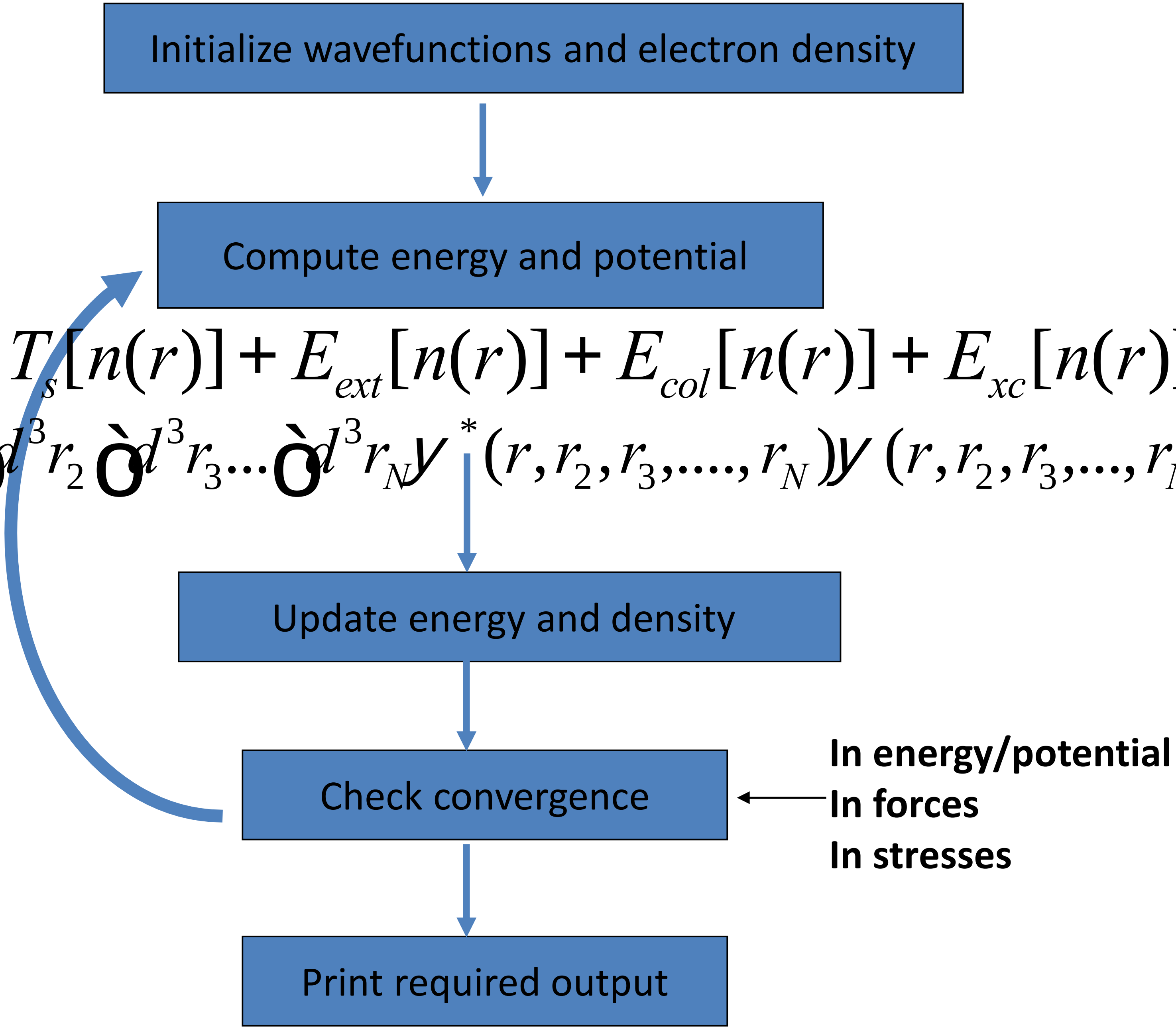




$$E_{xc} = \int n(r)\varepsilon_{xc}(r)dr$$

$$E_{xc} = \int n(r)\varepsilon_{xc}(r,\Delta r)dr$$

Flowchart of a standard DFT calculation



Initialize wavefunctions and electron density

Compute energy and potential

$$E[n(r)] = T_s[n(r)] + E_{ext}[n(r)] + E_{col}[n(r)] + E_{xc}[n(r)]$$

$$n(r) = N\int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \psi^*(r,r_2,r_3,\ldots,r_N)\psi(r,r_2,r_3,\ldots,r_N)$$

Update energy and density

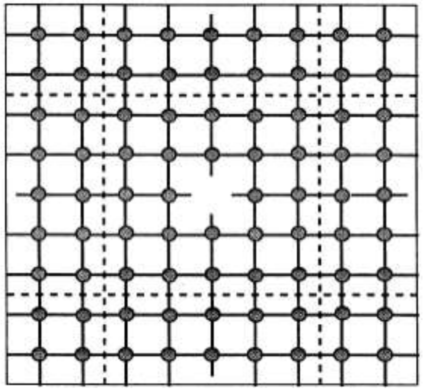
Check convergence

In energy/potential
In forces
In stresses

Print required output

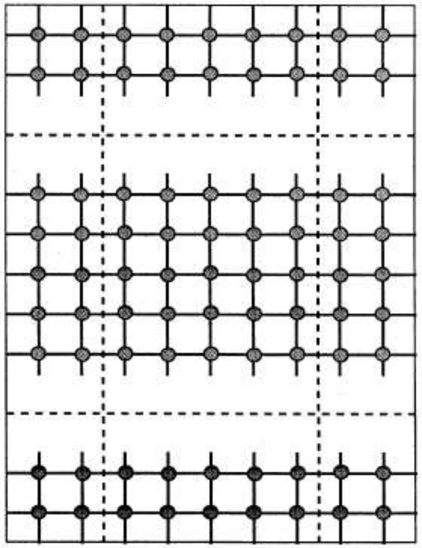
Crystal structure – non-periodic systems

Point-defect

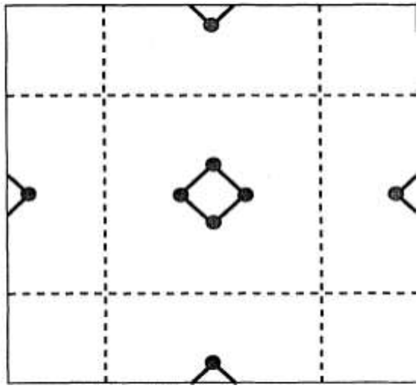


“big enough”

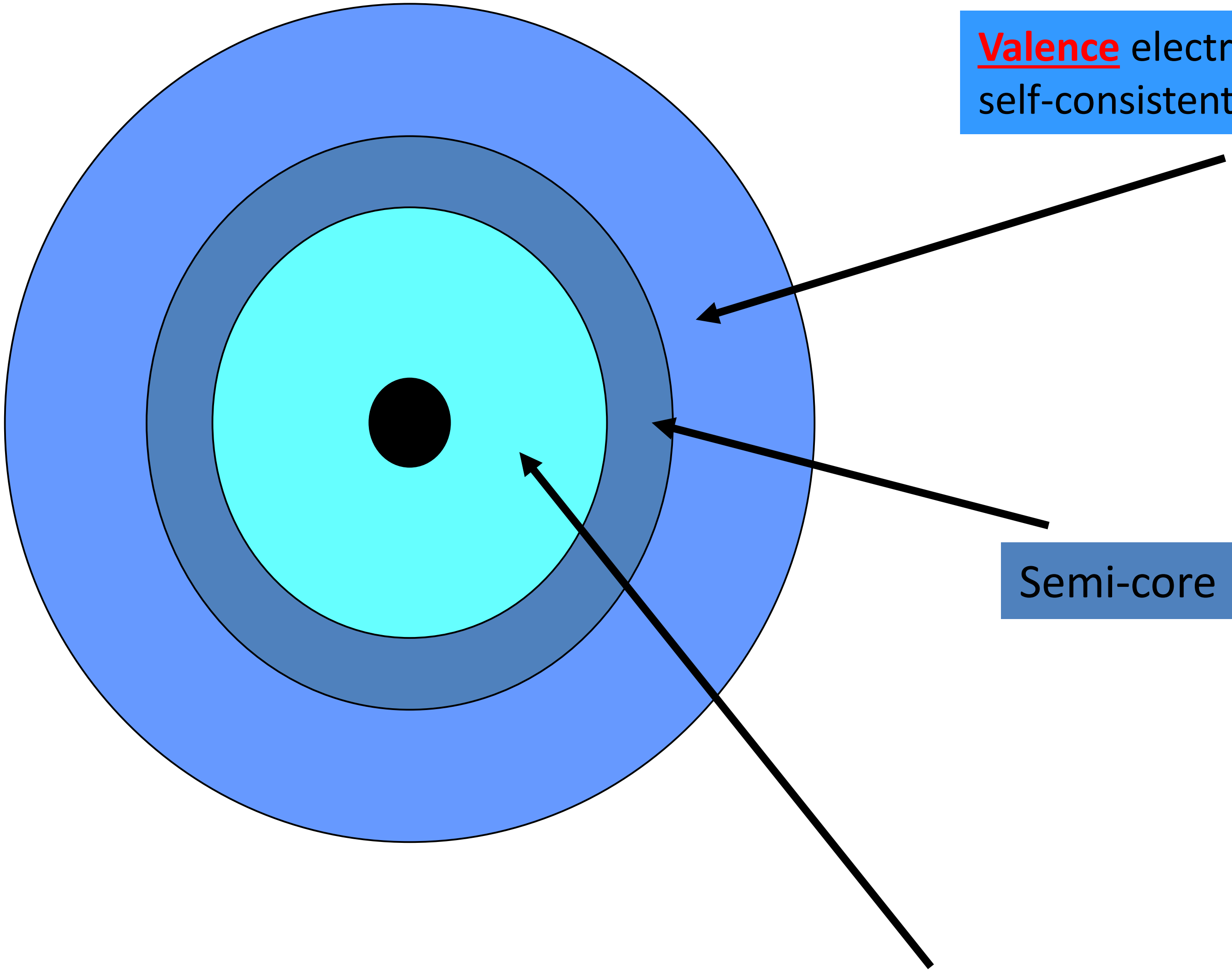
Surface



Molecule



Input key parameters - pseudopotentials



Valence electrons computed self-consistently

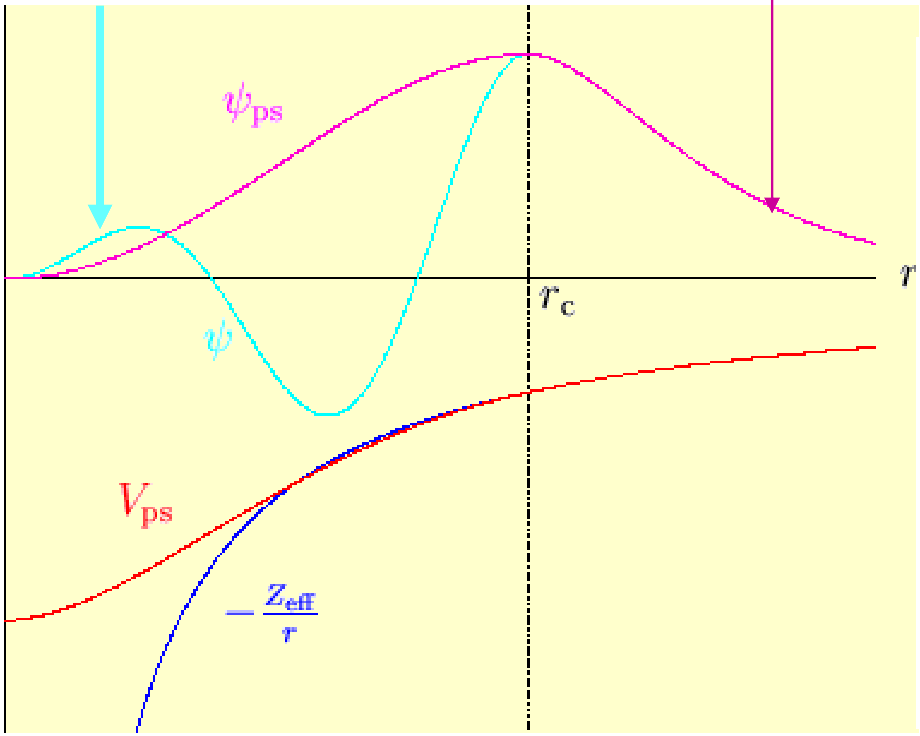
Semi-core states

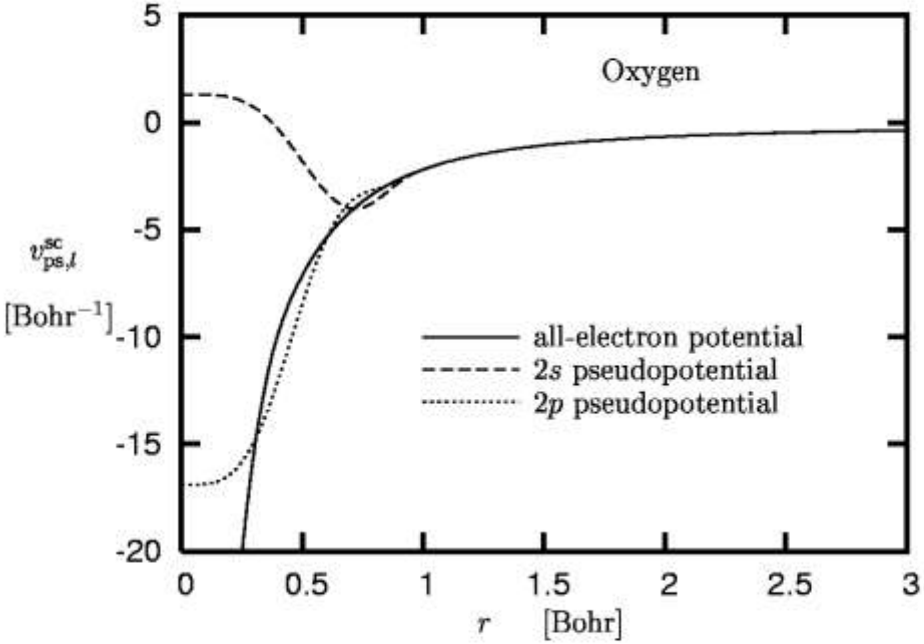
Core electrons ⇔ pseudopotential

Input key parameters - pseudopotentials

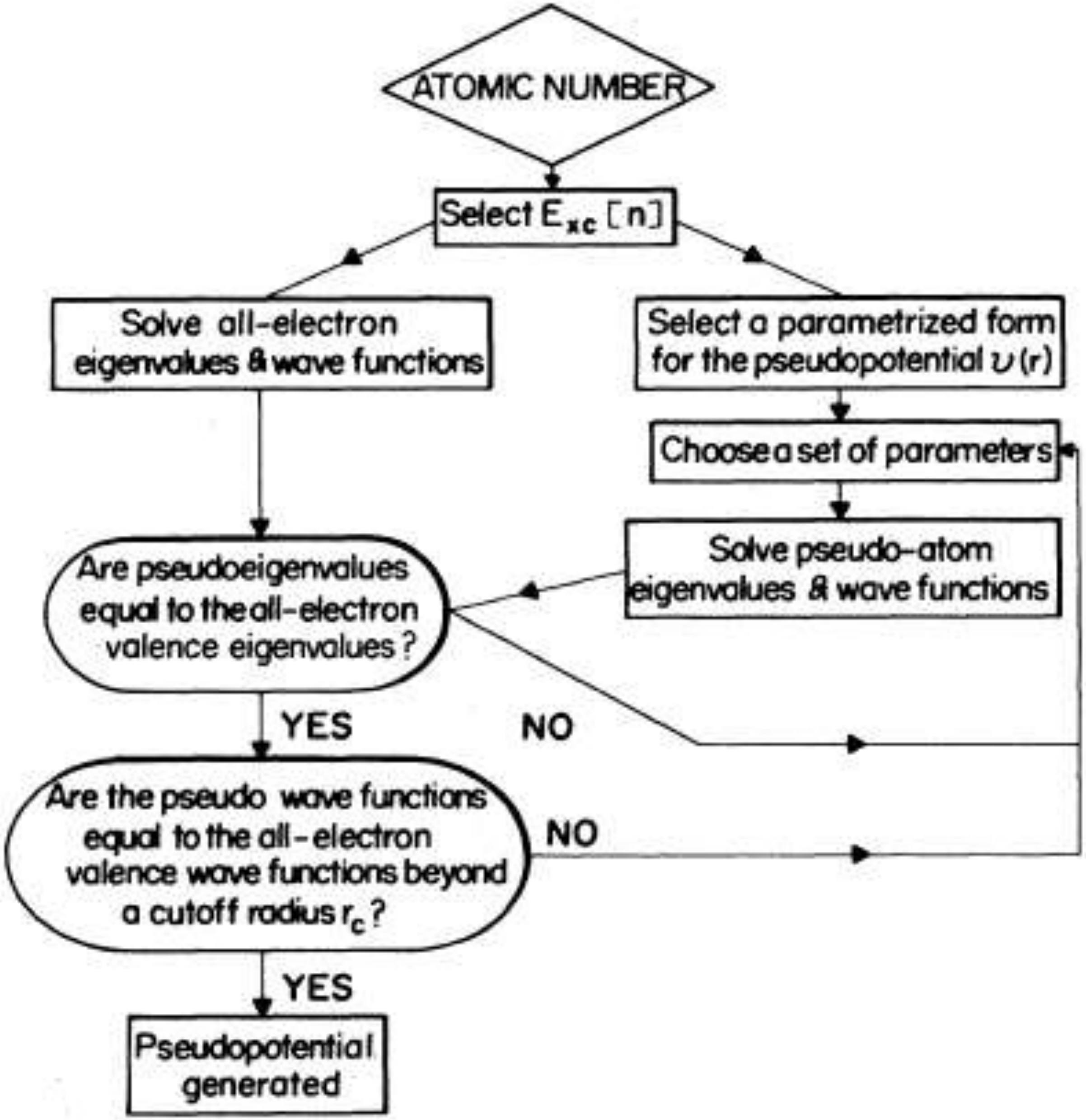
Pseudo-wavefunction

All electron wavefunction

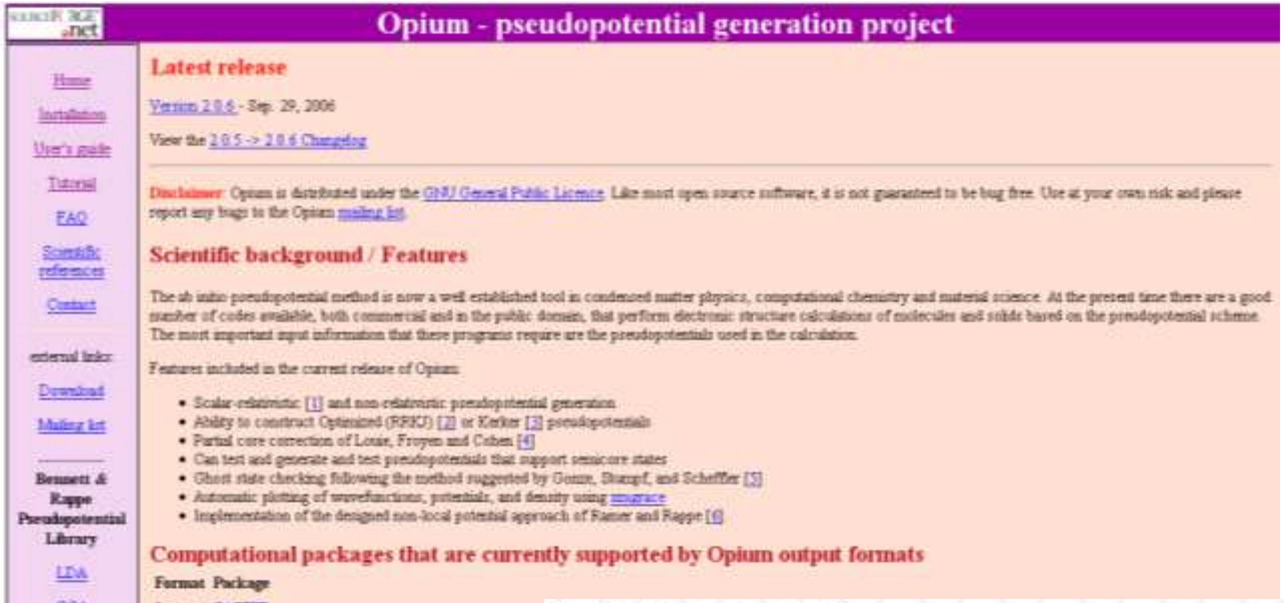




Input key parameters - pseudopotentials



Input key parameters - pseudopotentials



Opium - pseudopotential generation project

Home
Installation
User's guide
Tutorial
FAQ
Scientific references
Contact

external links:
Download
Mailing list

Bennett & Rappe Pseudopotential Library
LDA
GGA

Latest release

Version 2.0.6 - Sep. 29, 2006

View the 2.0.5 -> 2.0.6 Changelog

Disclaimer: Opium is distributed under the GNU General Public Licence. Like most open source software, it is not guaranteed to be bug free. Use at your own risk and please report any bugs to the Opium mailing list.

Scientific background / Features

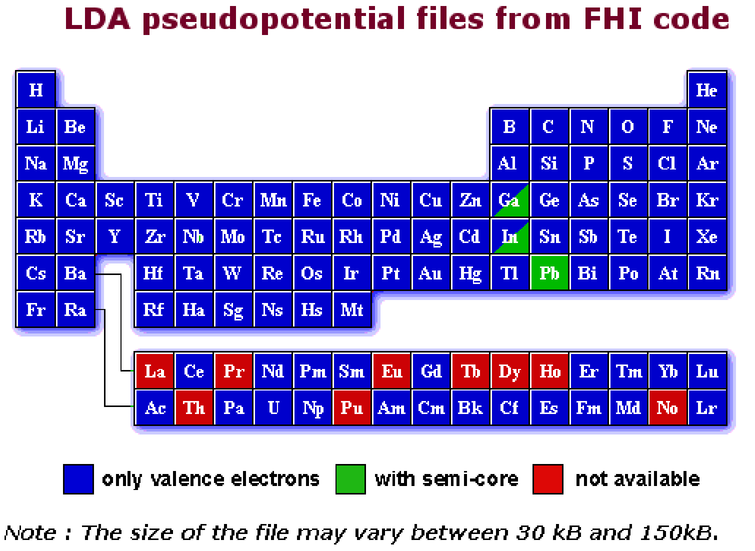
The ab initio pseudopotential method is now a well established tool in condensed matter physics, computational chemistry and material science. At the present time there are a good number of codes available, both commercial and in the public domain, that perform electronic structure calculations of molecules and solids based on the pseudopotential scheme. The most important input information that these programs require are the pseudopotentials used in the calculation.

Features included in the current release of Opium:

- Scalar-relativistic [1] and non-relativistic pseudopotential generation
- Ability to construct Optimized (RRKJ) [2] or Kerker [3] pseudopotentials
- Partial core correction of Louie, Froyen and Cohen [4]
- Can test and generate and test pseudopotentials that support semicore states
- Ghost state checking following the method suggested by Gonze, Stumpf, and Scheffler [5]
- Automatic plotting of wavefunctions, potentials, and density using xmgrace
- Implementation of the designed non-local potential approach of Ramer and Rappe [6]

Computational packages that are currently supported by Opium output formats

Format	Package
*.recpot	CASTEP
*.fhi	ABINIT
*.ncpp	PWSCF
*.pwf	Bh



LDA pseudopotential files from FHI code

H 🟦																	He 🟦
Li 🟦	Be 🟦											B 🟦	C 🟦	N 🟦	O 🟦	F 🟦	Ne 🟦
Na 🟦	Mg 🟦											Al 🟦	Si 🟦	P 🟦	S 🟦	Cl 🟦	Ar 🟦
K 🟦	Ca 🟦	Sc 🟦	Ti 🟦	V 🟦	Cr 🟦	Mn 🟦	Fe 🟦	Co 🟦	Ni 🟦	Cu 🟦	Zn 🟦	Ga 🟦🟩	Ge 🟦	As 🟦	Se 🟦	Br 🟦	Kr 🟦
Rb 🟦	Sr 🟦	Y 🟦	Zr 🟦	Nb 🟦	Mo 🟦	Tc 🟦	Ru 🟦	Rh 🟦	Pd 🟦	Ag 🟦	Cd 🟦	In 🟦🟩	Sn 🟦	Sb 🟦	Te 🟦	I 🟦	Xe 🟦
Cs 🟦	Ba 🟦		Hf 🟦	Ta 🟦	W 🟦	Re 🟦	Os 🟦	Ir 🟦	Pt 🟦	Au 🟦	Hg 🟦	Tl 🟦	Pb 🟩	Bi 🟦	Po 🟦	At 🟦	Rn 🟦
Fr 🟦	Ra 🟦		Rf 🟦	Ha 🟦	Sg 🟦	Ns 🟦	Hs 🟦	Mt 🟦									
			La 🟥	Ce 🟦	Pr 🟥	Nd 🟦	Pm 🟦	Sm 🟦	Eu 🟥	Gd 🟦	Tb 🟥	Dy 🟥	Ho 🟥	Er 🟦	Tm 🟦	Yb 🟦	Lu 🟦
			Ac 🟦	Th 🟥	Pa 🟦	U 🟦	Np 🟦	Pu 🟥	Am 🟦	Cm 🟦	Bk 🟦	Cf 🟦	Es 🟦	Fm 🟦	Md 🟦	No 🟥	Lr 🟦

🟦 only valence electrons 🟩 with semi-core 🟥 not available

Note : The size of the file may vary between 30 kB and 150kB.

The fhi98PP pseudopotential program

The package fhi98PP [1] in the present update of 27-06-03 allows one to

- Generate norm-conserving pseudopotentials of the Hamann [2] and Troullier-Martins [3] types, employing common parameterizations of the local-density approximation and generalized gradient approximations for exchange and correlation.

- Check the transferability of one's pseudopotentials, in particular to search for unphysical ghost states of their fully separable (Kleinman-Bylander) representation [4].

- Spin-polarized atoms can be calculated, and pseudopotentials for exact Kohn-Sham exchange calculations can be produced. These features are at a developmental stage and require care.

A database of generic input data files for most elements is part of this package. General background about pseudopotentials and practical considerations for generating them may be found in [1]. A hands-on tutorial and worked-out examples are available as well.

Unix c-shell scripts serve as command-line interfaces to facilitate the above tasks. Their pseudopotential output is compatible with the input format of the fhimd program [5] and can be readily adjusted to fit other codes. For visual inspection of results, these scripts provide graphics files to be viewed with the public domain plotting tool XMGRACE.

Download

The source distribution is available from the download page.

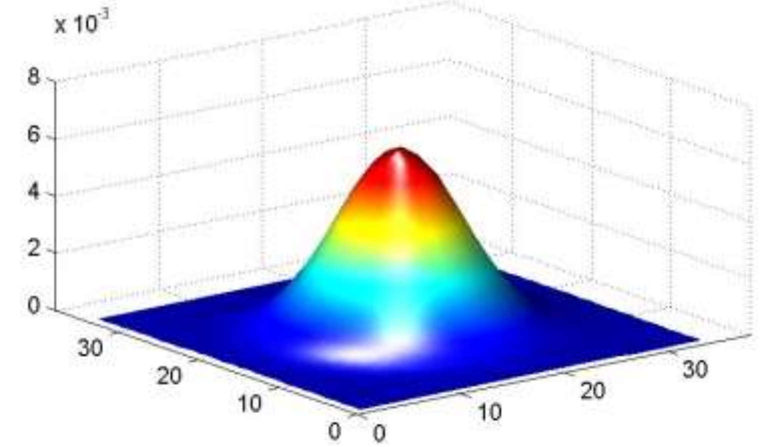
References

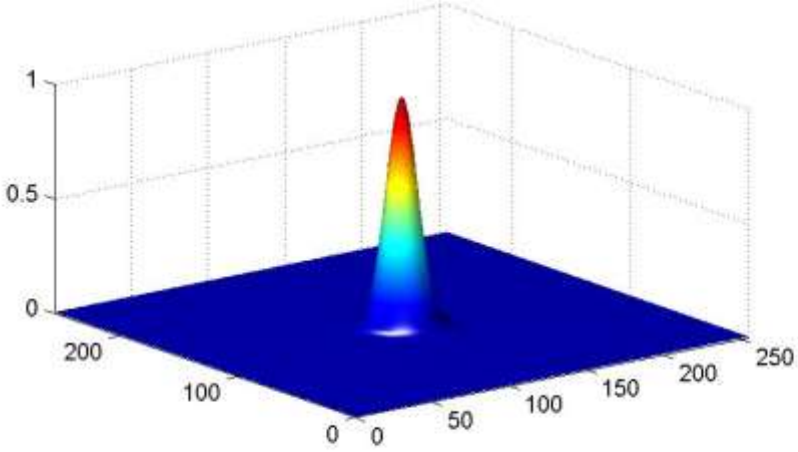
1. M. Fuchs, M. Scheffler, Comput. Phys. Commun., Comput. Phys. Commun. 119, 67-98 (1999),
   "Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory"
   [pdf (reprint)]
   [abs src ps], European mirror: [abs src ps]
2. D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).
3. N. Troullier, J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
4. X. Gonze, R. Stumpf, M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
5. M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler, Comput. Phys. Commun., **107**, 187 (1997).
   [pdf (reprint)]
   [abs src ps], European mirror: [abs src ps]

Home page of the Theory Department of FHI

Last modified: Fri Aug 1 15:00:00 METDST 2003

localized basis





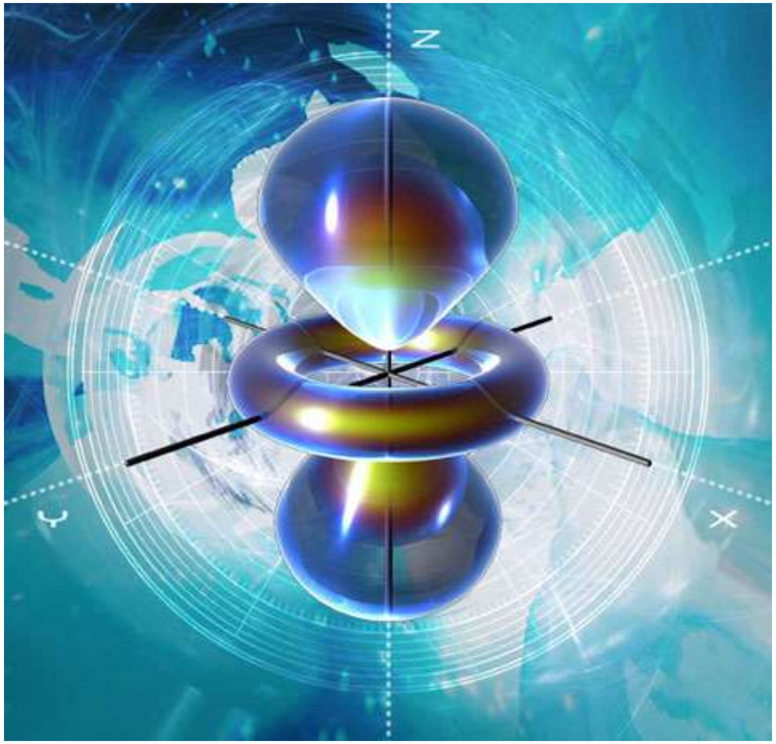
The number of gaussian functions summed to describe the inner shell orbital

The number of gaussian functions summed in the second STO

3-21G

The number of gaussian functions that comprise the first STO of the double zeta

```
CARBON      !(6S,3P) -> [3S,2P]
S 3
1        172.256000        0.617669000E-01
2        25.9109000        0.358794000
3        5.53335000        0.700713000
L 2
1        3.66498000        -0.395897000        0.23640000
2        0.770545000       1.21584000          0.860619000
L 1
1        0.195857000       1.00000000          1.00000000
```



planewaves

wavelength

$\lambda = 2\pi/G$

frequency

$f = \omega/2\pi$

period

$T = 1/f = 2\pi/\omega$

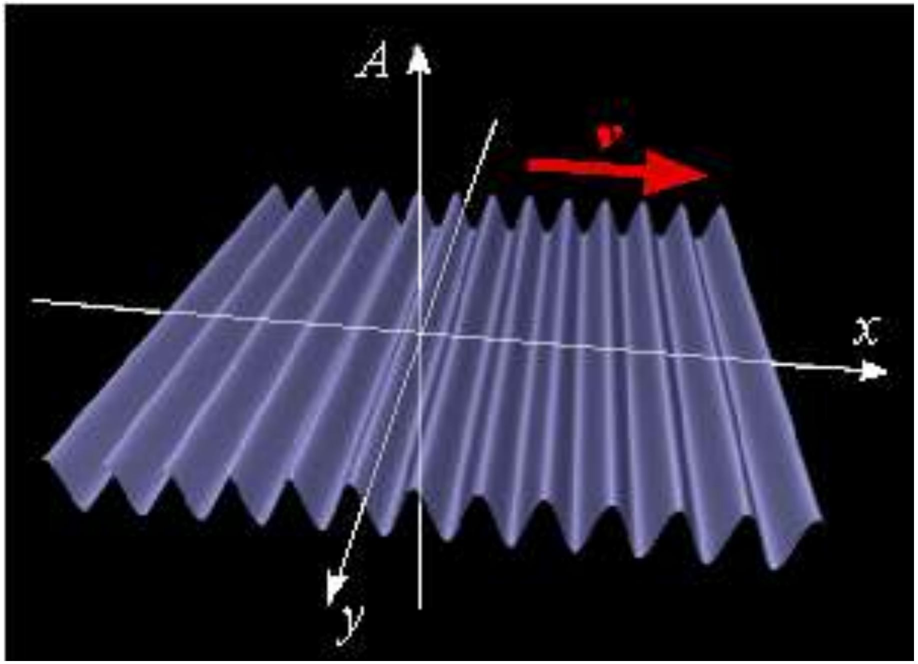
velocity

$v = \lambda/T = \omega/k$

Planewaves are characterized by their

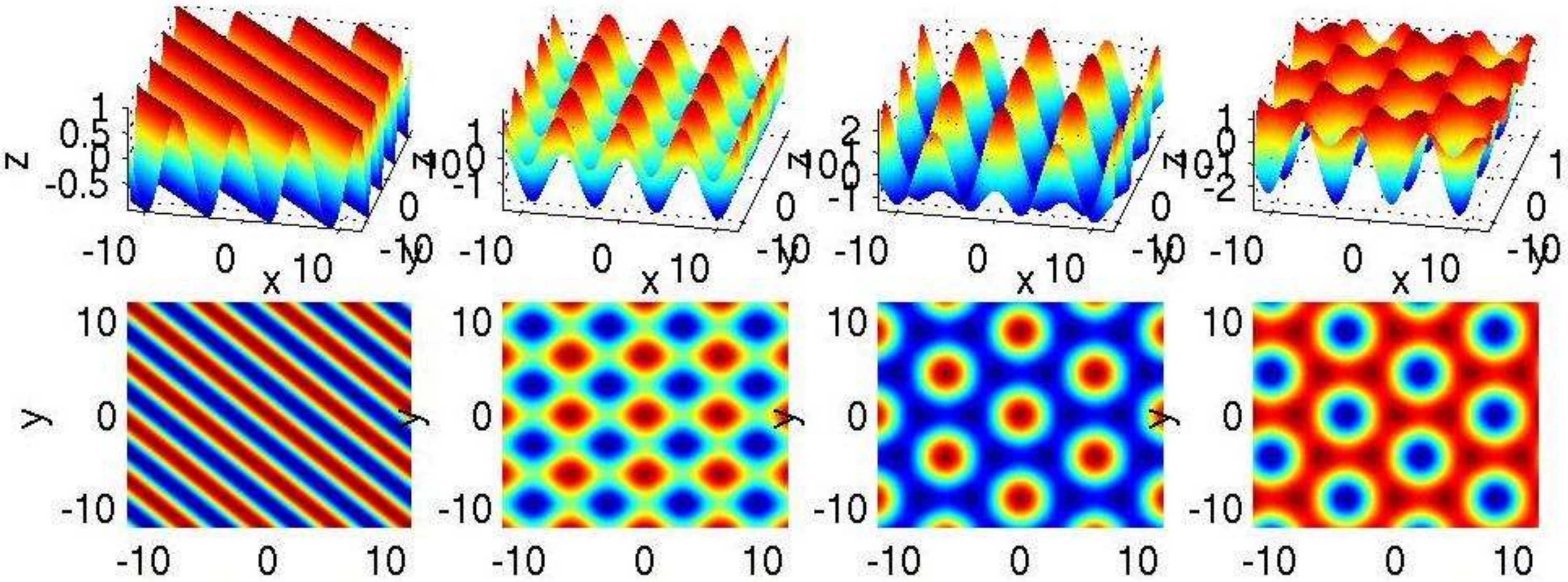
wavevector **G** →

angular speed ω



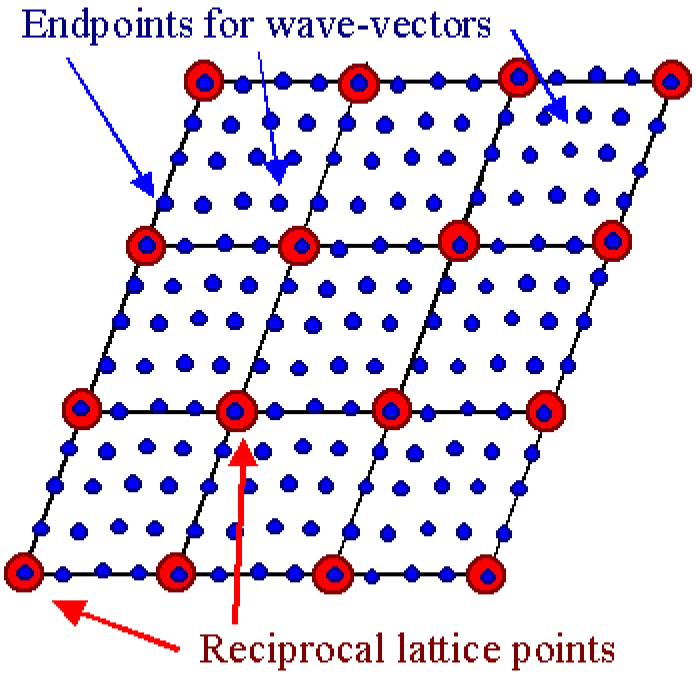
planewaves

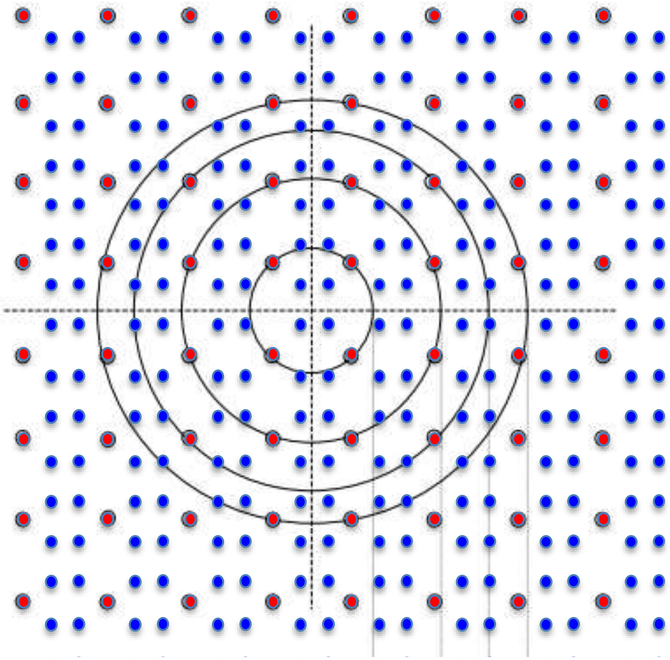
The electron density is obtained by superposition of planewaves

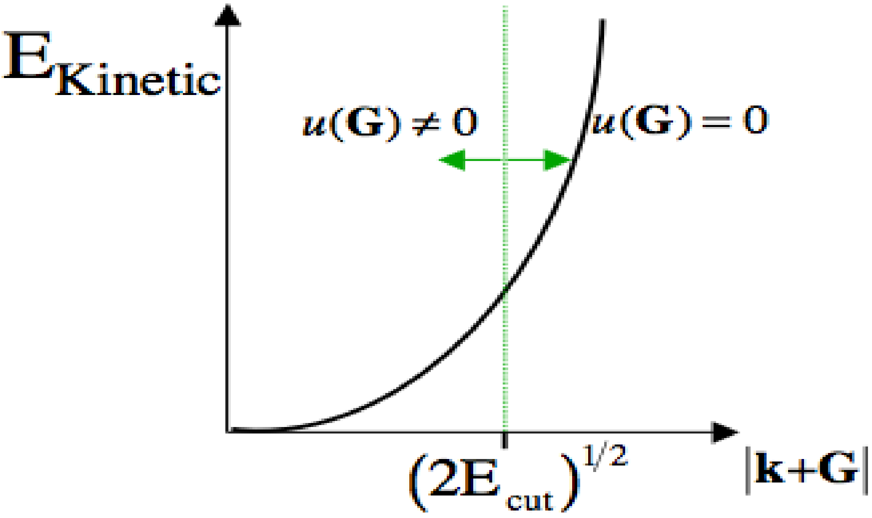


Input key parameters - K-points

$$\psi_i^{k}(r)$$ ⟸ Limited set of k points ~ boundary conditions







after: http://www.psi-k.org/Psik-training/Gonze-1.pdf

PRACTICAL ASPECTS: Properties

Electronic properties: electronic band structure, orbital energies, chemical bonding, hybridization, insulator/metallic character, Fermi surface, X-ray diffraction diagrams

Structural properties: crystal structures, prediction of structures under extreme conditions, prediction of phase transitions, analysis of hypothetical structures

Mechanical properties: elasticity, compressibility

Dielectric properties: hybridizations, atomic dynamic charges, dielectric susceptibilities, polarization, non-linear optical coefficients, piezoelectric tensor

Spectroscopic properties: Raman and Infrared active modes, silent modes, symmetry analysis of these modes

Dynamical properties: phonons, lattice instabilities, prediction of structures, study of phase transitions, thermodynamic properties, electron-phonon coupling

Values of the parameters

How to choose between LDA and GGA ?

- relatively homogeneous systems LDA

- highly inhomogeneous systems GGA

- elements from “p” bloc LDA

- transitional metals GGA

- LDA **under**estimates volume and distances

- GGA **over**estimates volume and distances

- best: try both: you bracket the experimental value

Values of the parameters

How to choose pseudopotentials ?

- the pseudopotential must be for the same XC as the calculation

- preferably start with a Troullier-Martins-type

- if it does not work try more advanced schemes

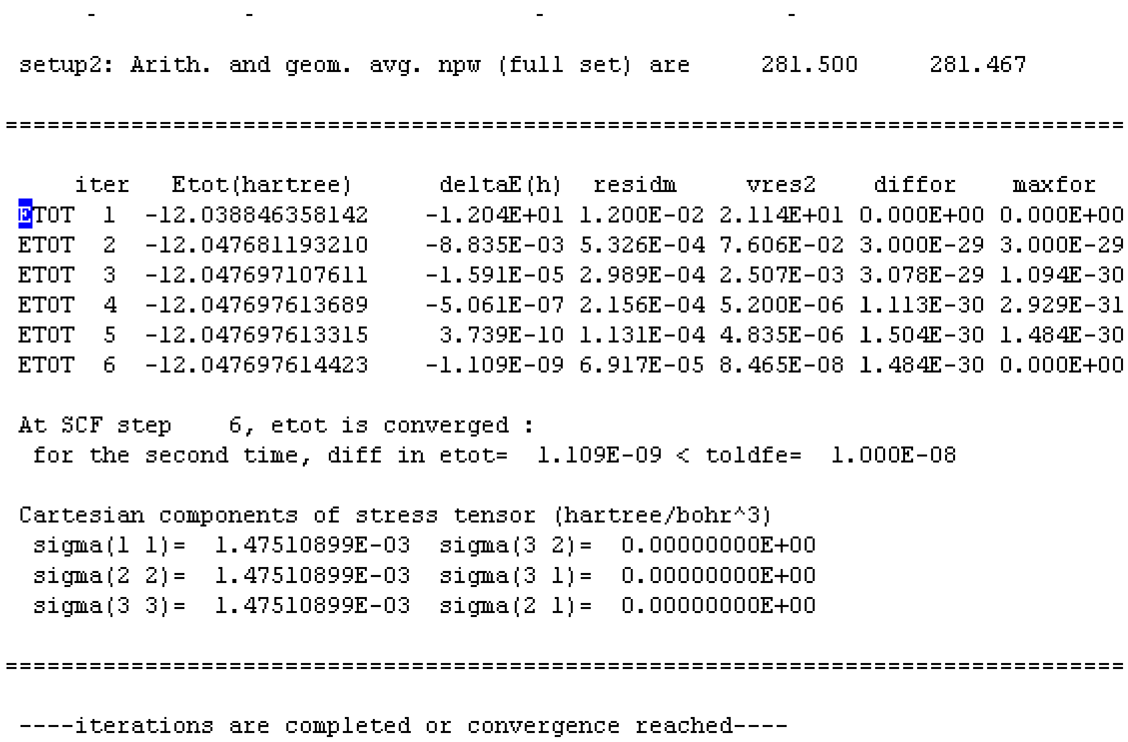
- check semi-core states

- check structural parameters for the compound not element!

Values of the parameters

How to choose no. of planewaves and k-points ?

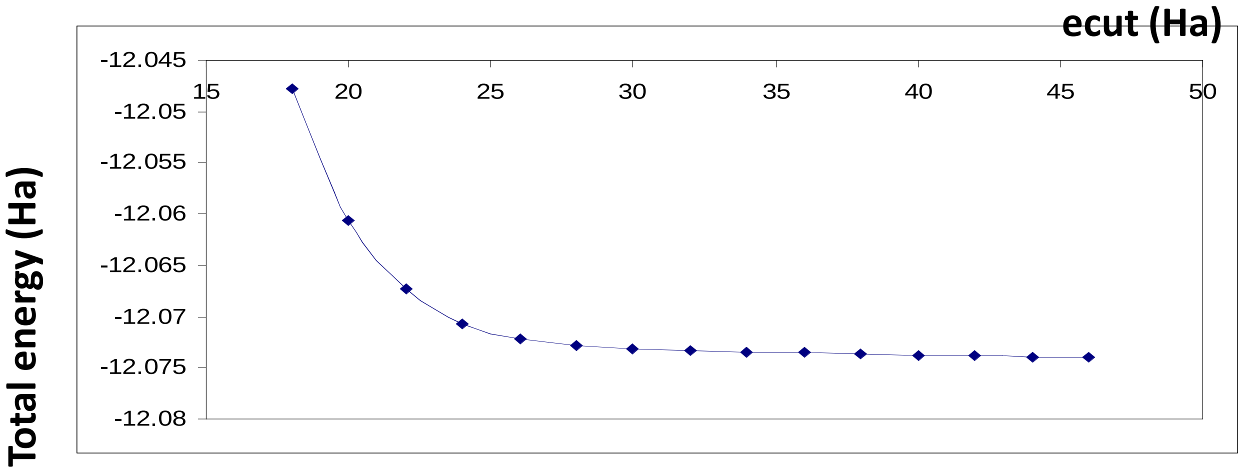
- check CONVERGENCE of the physical properties

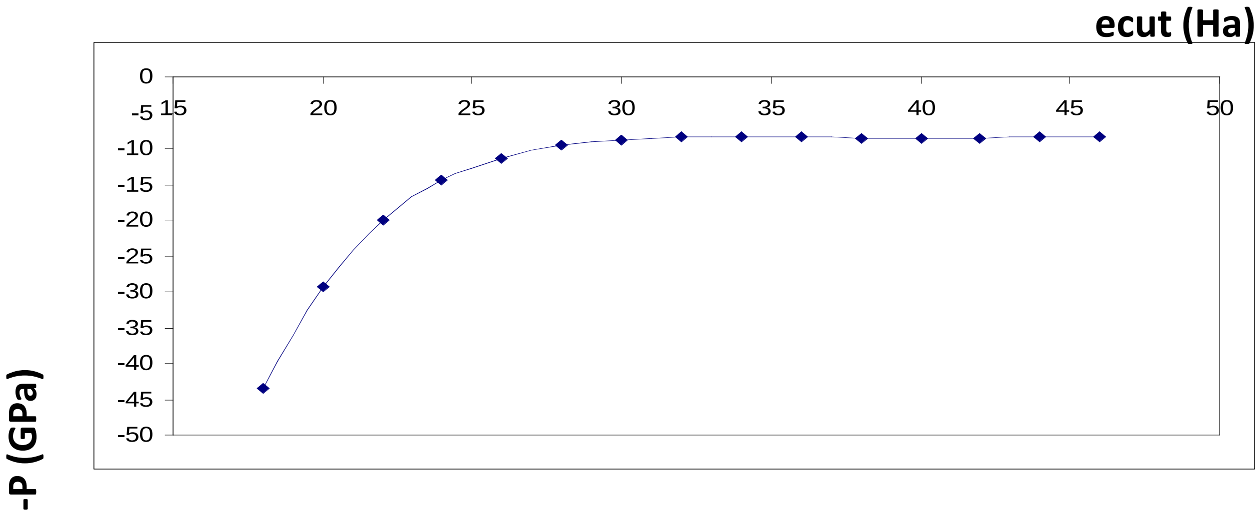


```
      -           -                   -                -

 setup2: Arith. and geom. avg. npw (full set) are     281.500     281.467

================================================================================

     iter   Etot(hartree)       deltaE(h)  residm     vres2    diffor    maxfor
 ETOT  1  -12.038846358142    -1.204E+01 1.200E-02 2.114E+01 0.000E+00 0.000E+00
 ETOT  2  -12.047681193210    -8.835E-03 5.326E-04 7.606E-02 3.000E-29 3.000E-29
 ETOT  3  -12.047697107611    -1.591E-05 2.989E-04 2.507E-03 3.078E-29 1.094E-30
 ETOT  4  -12.047697613689    -5.061E-07 2.156E-04 5.200E-06 1.113E-30 2.929E-31
 ETOT  5  -12.047697613315     3.739E-10 1.131E-04 4.835E-06 1.504E-30 1.484E-30
 ETOT  6  -12.047697614423    -1.109E-09 6.917E-05 8.465E-08 1.484E-30 0.000E+00

 At SCF step    6, etot is converged :
  for the second time, diff in etot=  1.109E-09 < toldfe=  1.000E-08

 Cartesian components of stress tensor (hartree/bohr^3)
  sigma(1 1)=  1.47510899E-03  sigma(3 2)=  0.00000000E+00
  sigma(2 2)=  1.47510899E-03  sigma(3 1)=  0.00000000E+00
  sigma(3 3)=  1.47510899E-03  sigma(2 1)=  0.00000000E+00

================================================================================

 ----iterations are completed or convergence reached----
```

Values of the parameters

- check CONVERGENCE of the physical properties





Usual output of calculations (in ABINIT)

Log (=STDOUT) file
- detailed information about the run; energies, forces, errors, warnings,etc.

Output file:
- simplified “clear” output:
  - full list of run parameters
  - total energy; electronic band eigenvalues; pressure; magnetization, etc.

Charge density = DEN

Electronic density of states = DOS

Analysis of the geometry = GEO

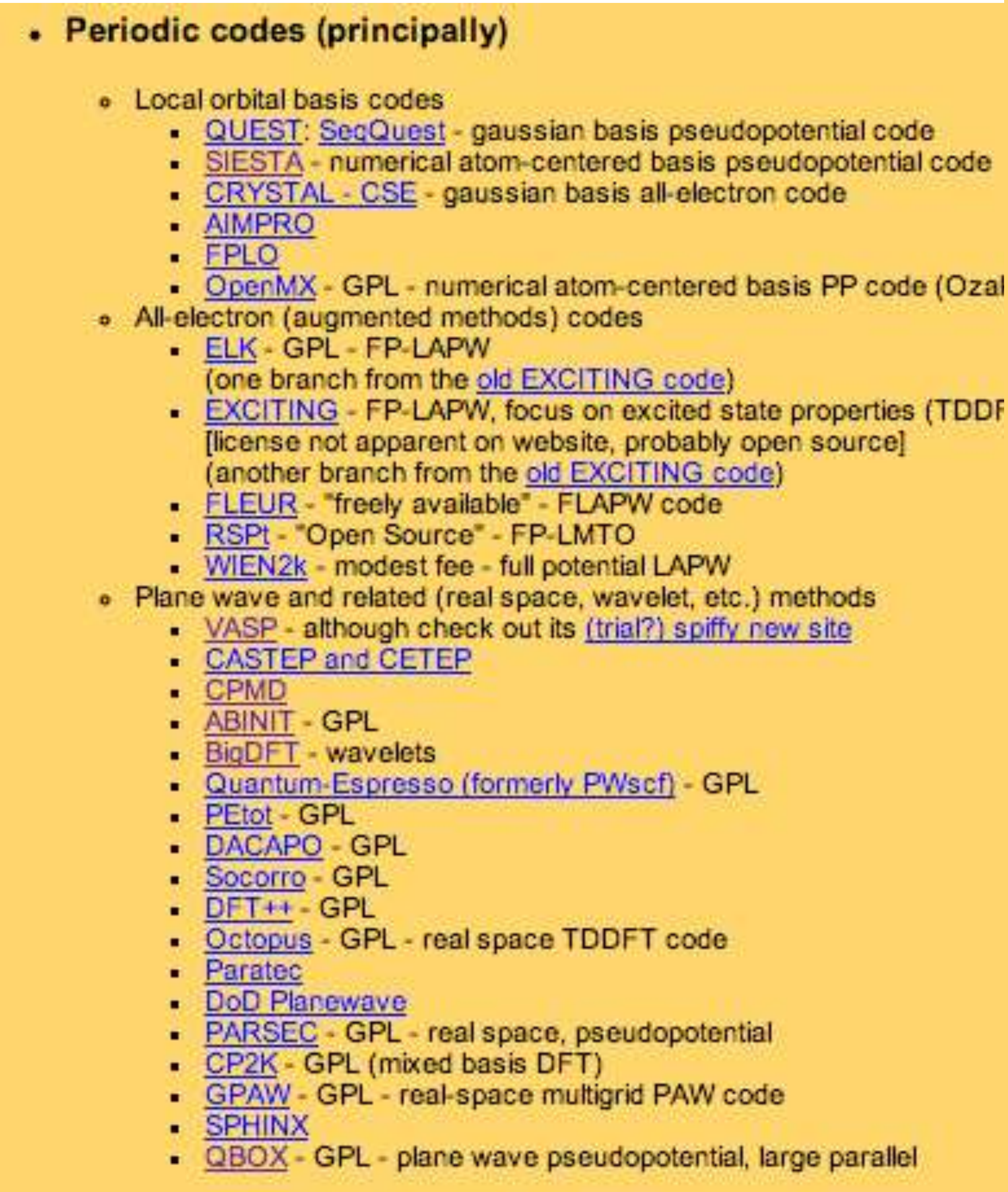
Wavefunctions = WFK, WFQ

Dynamical matrix = DDB

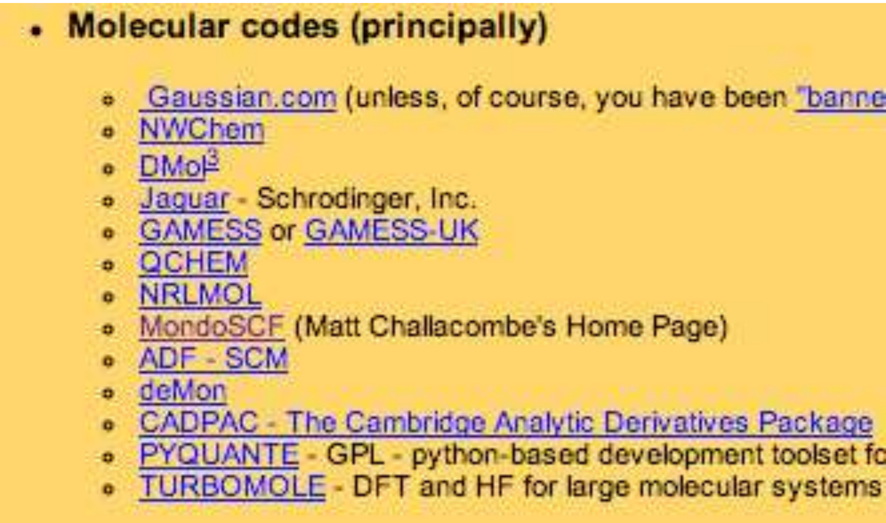
etc.

DFT codes

http://dft.sandia.gov/Quest/DFT_codes.html
http://www.psi-k.org/

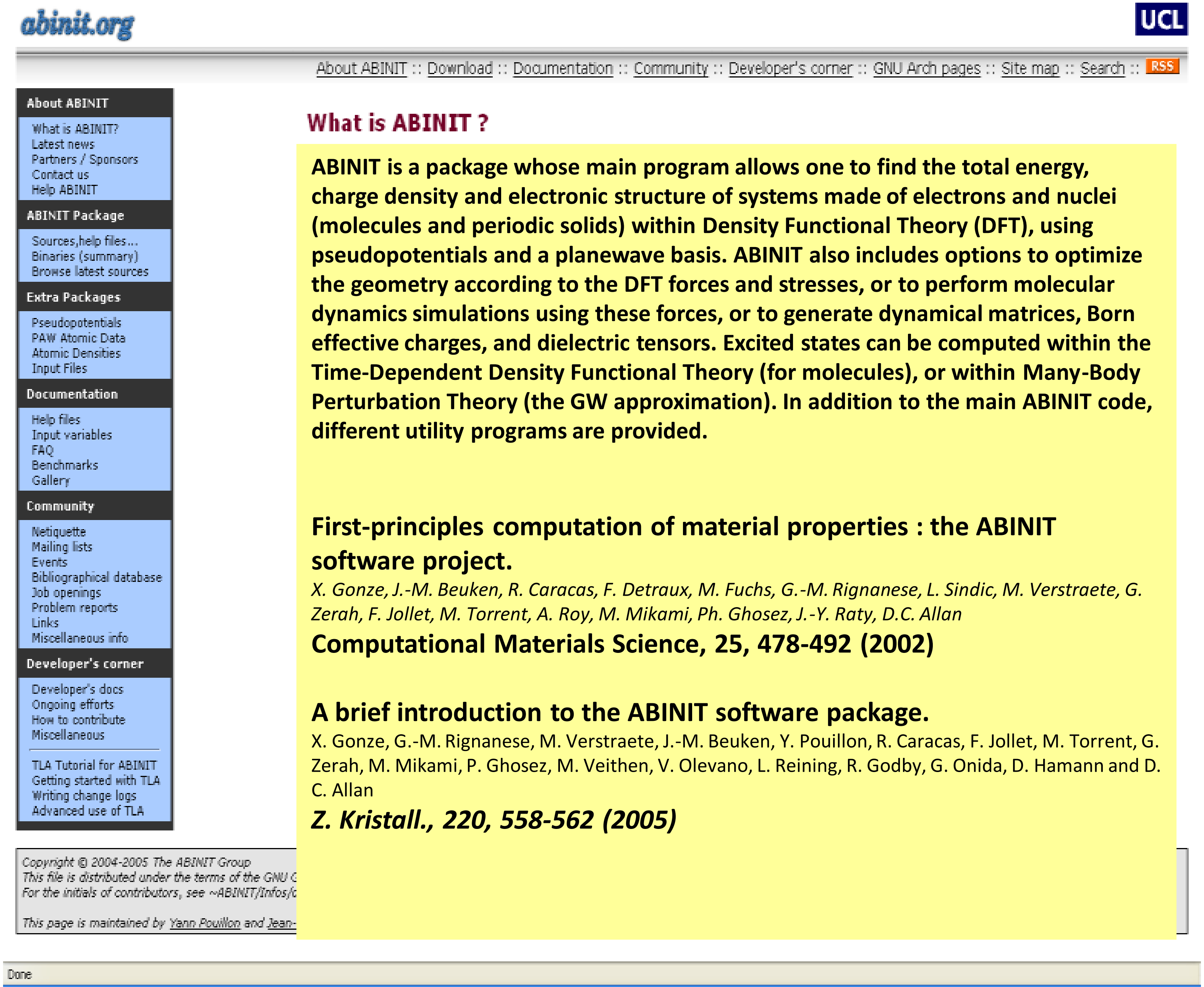


- **Periodic codes (principally)**
  - Local orbital basis codes
    - QUEST: SeqQuest - gaussian basis pseudopotential code
    - SIESTA - numerical atom-centered basis pseudopotential code
    - CRYSTAL - CSE - gaussian basis all-electron code
    - AIMPRO
    - FPLO
    - OpenMX - GPL - numerical atom-centered basis PP code (Ozal
  - All-electron (augmented methods) codes
    - ELK - GPL - FP-LAPW
      (one branch from the old EXCITING code)
    - EXCITING - FP-LAPW, focus on excited state properties (TDDF
      [license not apparent on website, probably open source]
      (another branch from the old EXCITING code)
    - FLEUR - "freely available" - FLAPW code
    - RSPt - "Open Source" - FP-LMTO
    - WIEN2k - modest fee - full potential LAPW
  - Plane wave and related (real space, wavelet, etc.) methods
    - VASP - although check out its (trial?) spiffy new site
    - CASTEP and CETEP
    - CPMD
    - ABINIT - GPL
    - BigDFT - wavelets
    - Quantum-Espresso (formerly PWscf) - GPL
    - PEtot - GPL
    - DACAPO - GPL
    - Socorro - GPL
    - DFT++ - GPL
    - Octopus - GPL - real space TDDFT code
    - Paratec
    - DoD Planewave
    - PARSEC - GPL - real space, pseudopotential
    - CP2K - GPL (mixed basis DFT)
    - GPAW - GPL - real-space multigrid PAW code
    - SPHINX
    - QBOX - GPL - plane wave pseudopotential, large parallel



- **Molecular codes (principally)**
  - Gaussian.com (unless, of course, you have been "banne
  - NWChem
  - DMol^3
  - Jaguar - Schrodinger, Inc.
  - GAMESS or GAMESS-UK
  - QCHEM
  - NRLMOL
  - MondoSCF (Matt Challacombe's Home Page)
  - ADF - SCM
  - deMon
  - CADPAC - The Cambridge Analytic Derivatives Package
  - PYQUANTE - GPL - python-based development toolset fo
  - TURBOMOLE - DFT and HF for large molecular systems

DFT codes: A B I N I T



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- Contact us
- Help ABINIT

ABINIT Package
- Sources,help files...
- Binaries (summary)
- Browse latest sources

Extra Packages
- Pseudopotentials
- PAW Atomic Data
- Atomic Densities
- Input Files

Documentation
- Help files
- Input variables
- FAQ
- Benchmarks
- Gallery

Community
- Netiquette
- Mailing lists
- Events
- Bibliographical database
- Job openings
- Problem reports
- Links
- Miscellaneous info

Developer's corner
- Developer's docs
- Ongoing efforts
- How to contribute
- Miscellaneous

- TLA Tutorial for ABINIT
- Getting started with TLA
- Writing change logs
- Advanced use of TLA

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For the initials of contributors, see ~ABINIT/Infos/c

This page is maintained by Yann Pouillon and Jean-

Done

What is ABINIT ?

ABINIT is a package whose main program allows one to find the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials and a planewave basis. ABINIT also includes options to optimize the geometry according to the DFT forces and stresses, or to perform molecular dynamics simulations using these forces, or to generate dynamical matrices, Born effective charges, and dielectric tensors. Excited states can be computed within the Time-Dependent Density Functional Theory (for molecules), or within Many-Body Perturbation Theory (the GW approximation). In addition to the main ABINIT code, different utility programs are provided.

First-principles computation of material properties : the ABINIT software project.

X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D.C. Allan

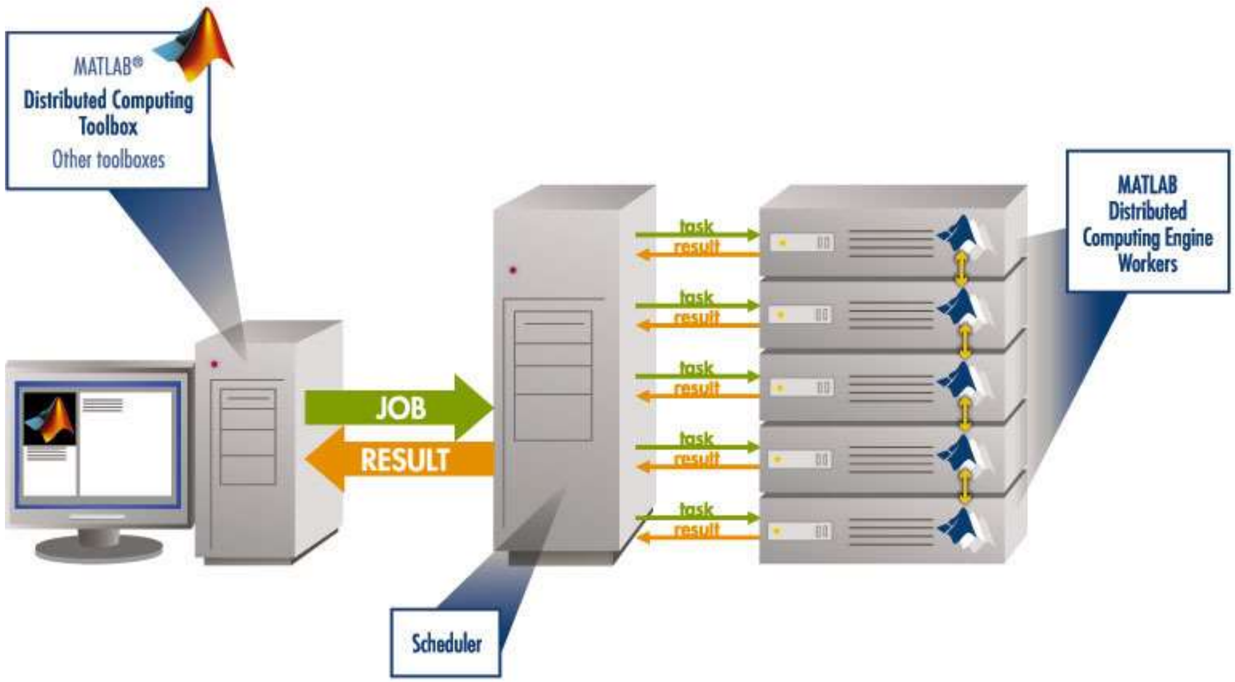
Computational Materials Science, 25, 478-492 (2002)

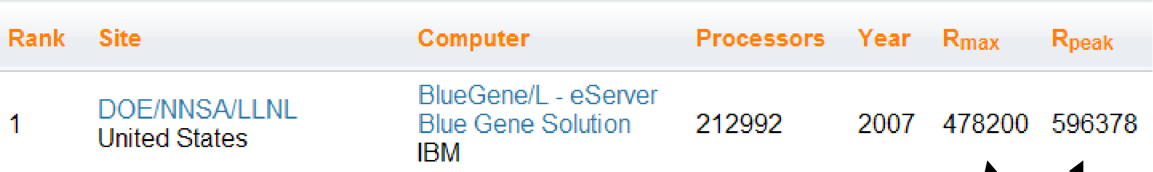
A brief introduction to the ABINIT software package.

X. Gonze, G.-M. Rignanese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, P. Ghosez, M. Veithen, V. Olevano, L. Reining, R. Godby, G. Onida, D. Hamann and D. C. Allan

Z. Kristall., 220, 558-562 (2005)

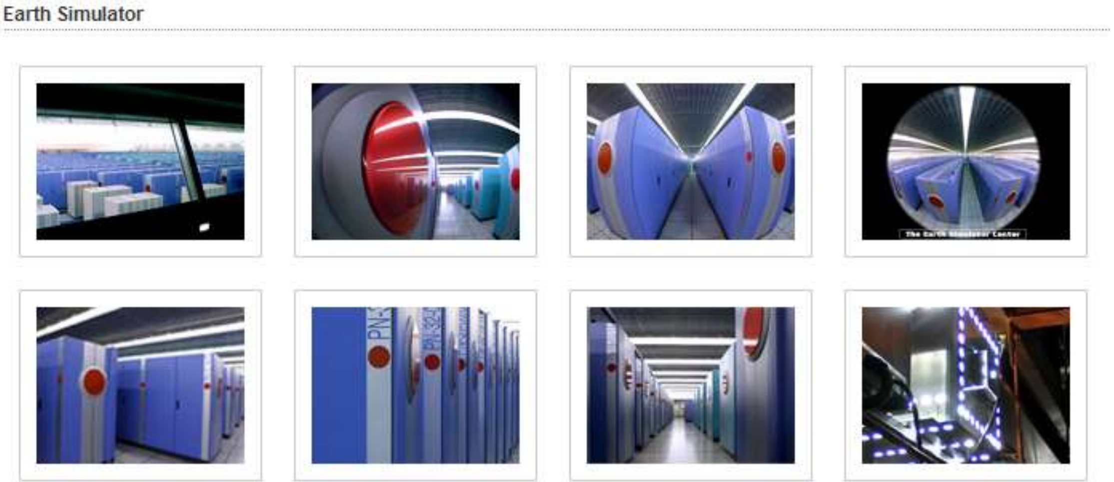
Sequential calculations ⇔ one processor at a time
Parallel calculations ⇔ several processors in the same time





Rank	Site	Computer	Processors	Year	R_{max}	R_{peak}
1	DOE/NNSA/LLNL United States	BlueGene/L - eServer Blue Gene Solution IBM	212992	2007	478200	596378

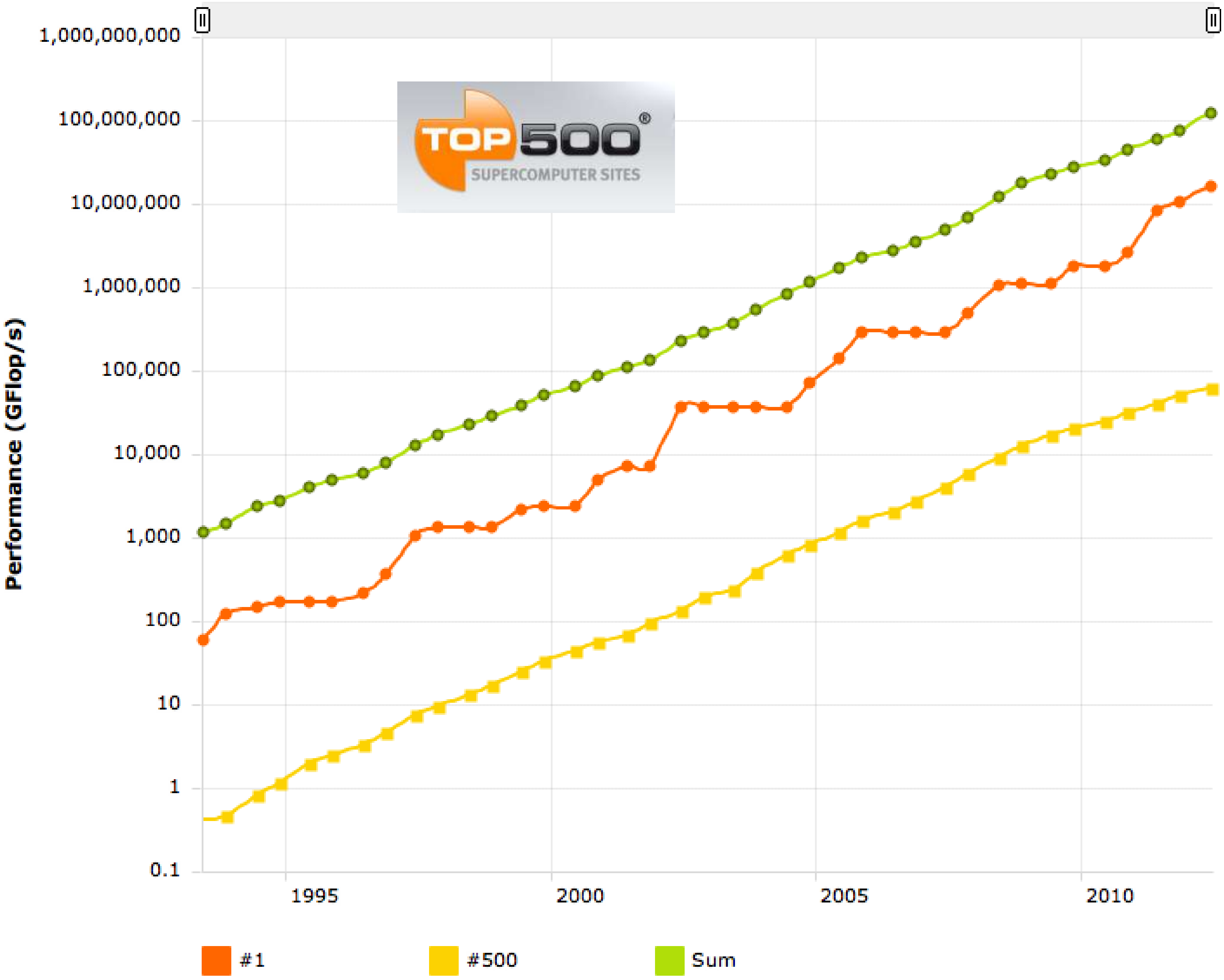
These are Gflops / second (~*0.5 petaflop*)
= millions of operations / second



Earth Simulator

1 flop = 1 floating point operation / cycle

Itanium 2 @ 1.5 GHz ~ 6Gflops/sec = $6*10^9$ operations/second


TOP500®
SUPERCOMPUTER SITES
Performance (GFlop/s)
1,000,000,000
100,000,000
10,000,000
1,000,000
100,000
10,000
1,000
100
10
1
0.1
1995
2000
2005
2010
#1
#500
Sum

Welcome to the Partnerships Online Proposal System

(You cannot view your proposal after the deadline un

What's new:

Systems: Steele Cluster (Purdue), Kraken Upgrac

See www.teragrid.org/userinfo/hardware/reso

Request "Advanced Support Program" (ASP) for scalability and/or integration into Science Gatewa

Guidelines for writing a successful gateway propo

New names: Startup/Educational Allocation has r Research Allocation request pool will not have the limited.

The Research Allocation request (proposal) docu requests greater than 10,000,000 SUs or Multi-ye

Welcome to POPS

The Consortium is happy to announce that the Transnational Access Programme will continue up to the end of 2012.

Next deadline for submitting applications is 15 November 2008.

All the applications submitted from now on will be selected by the new selection panel and, if accepted, funded under the HPC-EUROPA2 Project.

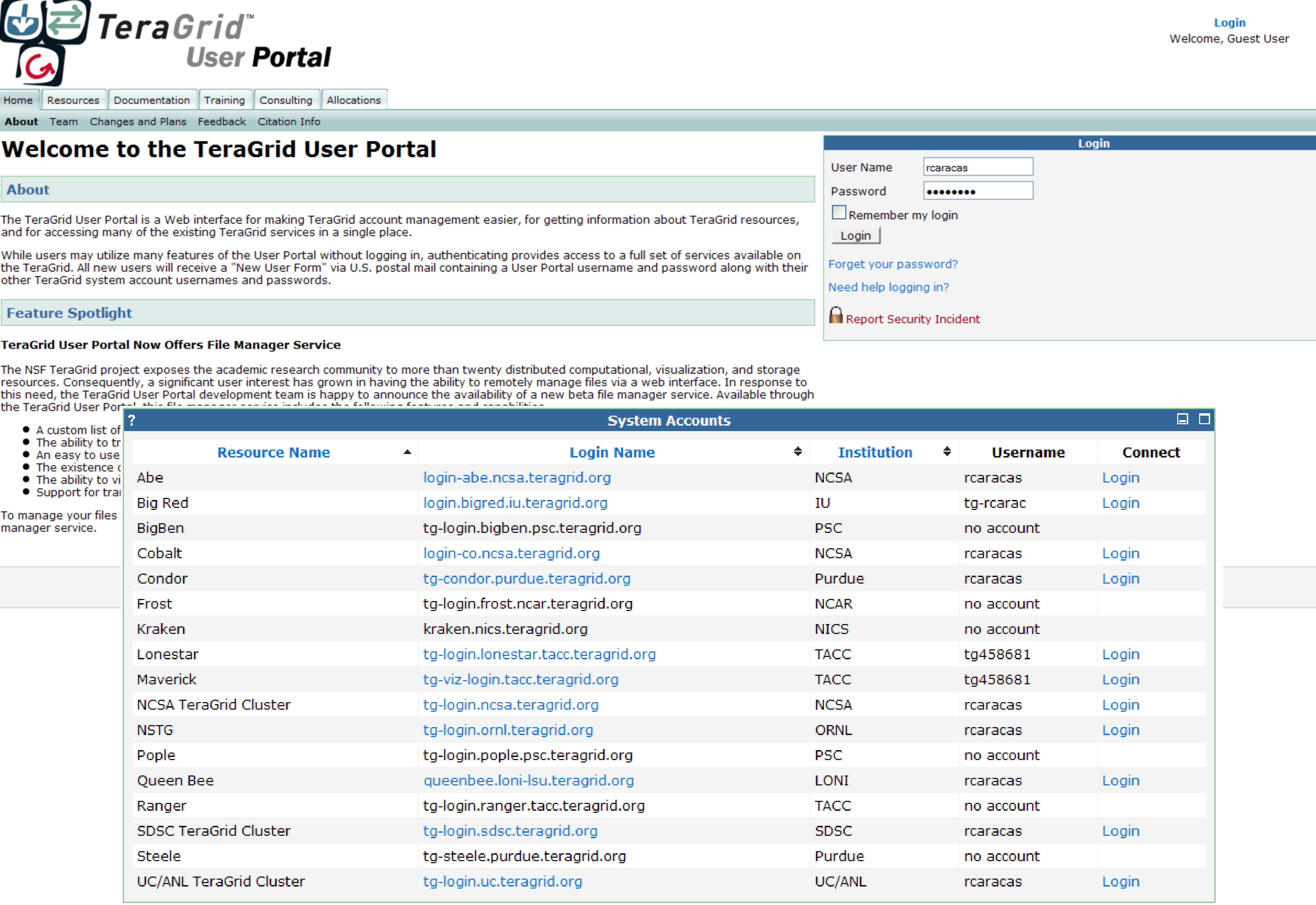
The whole project website will be renewed.

The rules for the Access are unchanged, but researchers can benefit from a greater allocation of computational resources.

Are you a scientist of postgraduate level or above, working in the EU or an Associated State?
Do you require large computing power to improve your research?
inland?

ntres: BSC
inland).

Transnational Access Programme will continue up to the end of 2012



Welcome to the TeraGrid User Portal

About

The TeraGrid User Portal is a Web interface for making TeraGrid account management easier, for getting information about TeraGrid resources, and for accessing many of the existing TeraGrid services in a single place.

While users may utilize many features of the User Portal without logging in, authenticating provides access to a full set of services available on the TeraGrid. All new users will receive a "New User Form" via U.S. postal mail containing a User Portal username and password along with their other TeraGrid system account usernames and passwords.

Feature Spotlight

TeraGrid User Portal Now Offers File Manager Service

The NSF TeraGrid project exposes the academic research community to more than twenty distributed computational, visualization, and storage resources. Consequently, a significant user interest has grown in having the ability to remotely manage files via a web interface. In response to this need, the TeraGrid User Portal development team is happy to announce the availability of a new beta file manager service. Available through the TeraGrid User Por

- A custom list of
- The ability to tr
- An easy to use
- The existence c
- The ability to vi
- Support for tra

To manage your files
manager service.

Login

User Name: rcaracas

Password: ••••••••

☐ Remember my login

Login

Forget your password?

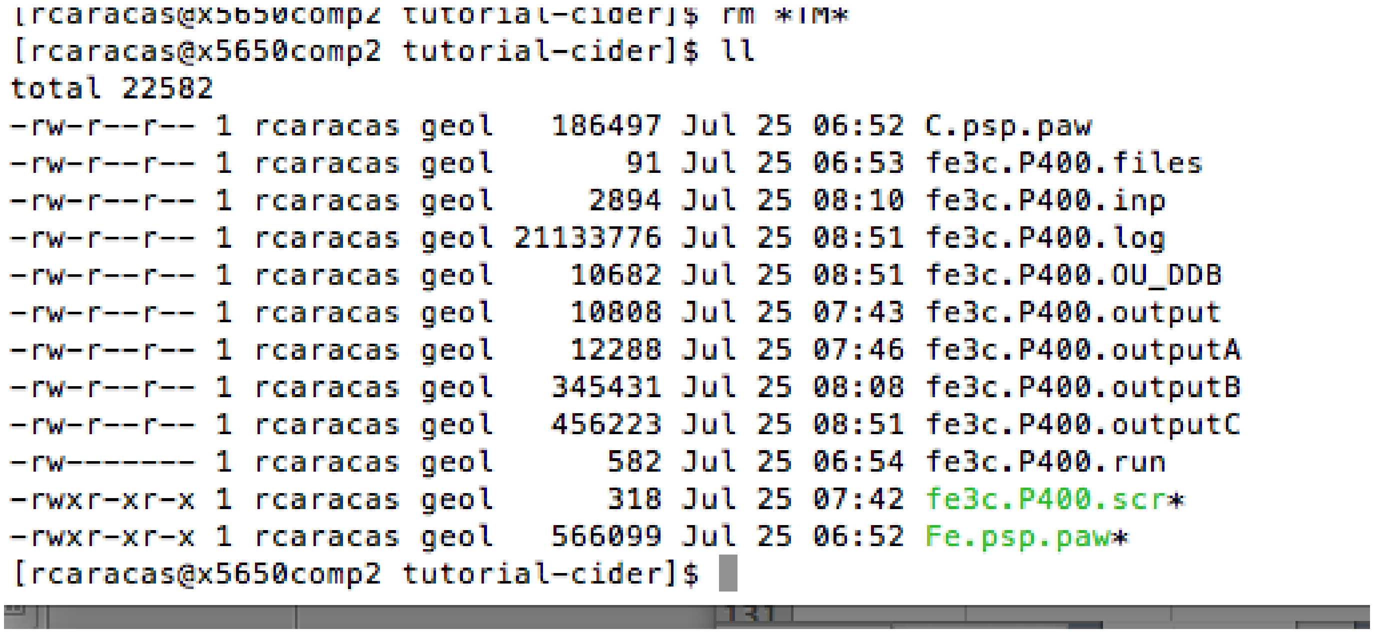
Need help logging in?

Report Security Incident

System Accounts

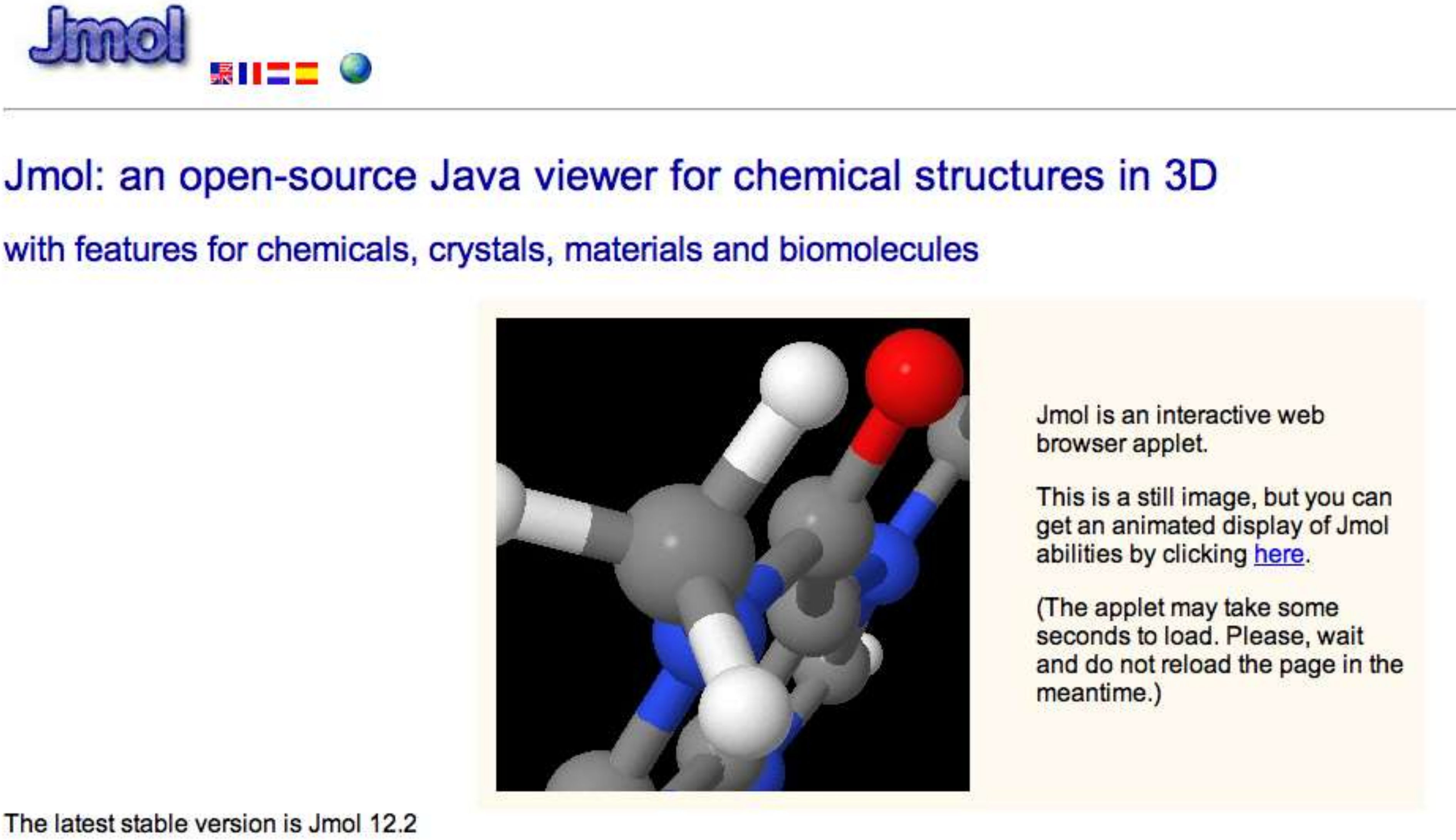
Resource Name	Login Name	Institution	Username	Connect
Abe	login-abe.ncsa.teragrid.org	NCSA	rcaracas	Login
Big Red	login.bigred.iu.teragrid.org	IU	tg-rcarac	Login
BigBen	tg-login.bigben.psc.teragrid.org	PSC	no account	
Cobalt	login-co.ncsa.teragrid.org	NCSA	rcaracas	Login
Condor	tg-condor.purdue.teragrid.org	Purdue	rcaracas	Login
Frost	tg-login.frost.ncar.teragrid.org	NCAR	no account	
Kraken	kraken.nics.teragrid.org	NICS	no account	
Lonestar	tg-login.lonestar.tacc.teragrid.org	TACC	tg458681	Login
Maverick	tg-viz-login.tacc.teragrid.org	TACC	tg458681	Login
NCSA TeraGrid Cluster	tg-login.ncsa.teragrid.org	NCSA	rcaracas	Login
NSTG	tg-login.ornl.teragrid.org	ORNL	rcaracas	Login
Pople	tg-login.pople.psc.teragrid.org	PSC	no account	
Queen Bee	queenbee.loni-lsu.teragrid.org	LONI	rcaracas	Login
Ranger	tg-login.ranger.tacc.teragrid.org	TACC	no account	
SDSC TeraGrid Cluster	tg-login.sdsc.teragrid.org	SDSC	rcaracas	Login
Steele	tg-steele.purdue.teragrid.org	Purdue	no account	
UC/ANL TeraGrid Cluster	tg-login.uc.teragrid.org	UC/ANL	rcaracas	Login

RUN MD CODE



```
[rcaracas@x5650comp2 tutorial-cider]$ rm *IM*
[rcaracas@x5650comp2 tutorial-cider]$ ll
total 22582
-rw-r--r-- 1 rcaracas geol   186497 Jul 25 06:52 C.psp.paw
-rw-r--r-- 1 rcaracas geol       91 Jul 25 06:53 fe3c.P400.files
-rw-r--r-- 1 rcaracas geol     2894 Jul 25 08:10 fe3c.P400.inp
-rw-r--r-- 1 rcaracas geol 21133776 Jul 25 08:51 fe3c.P400.log
-rw-r--r-- 1 rcaracas geol    10682 Jul 25 08:51 fe3c.P400.OU_DDB
-rw-r--r-- 1 rcaracas geol    10808 Jul 25 07:43 fe3c.P400.output
-rw-r--r-- 1 rcaracas geol    12288 Jul 25 07:46 fe3c.P400.outputA
-rw-r--r-- 1 rcaracas geol   345431 Jul 25 08:08 fe3c.P400.outputB
-rw-r--r-- 1 rcaracas geol   456223 Jul 25 08:51 fe3c.P400.outputC
-rw------- 1 rcaracas geol      582 Jul 25 06:54 fe3c.P400.run
-rwxr-xr-x 1 rcaracas geol      318 Jul 25 07:42 fe3c.P400.scr*
-rwxr-xr-x 1 rcaracas geol   566099 Jul 25 06:52 Fe.psp.paw*
[rcaracas@x5650comp2 tutorial-cider]$ 
```

Jmol exercise: http://jmol.sourceforge.net/



Jmol: an open-source Java viewer for chemical structures in 3D

with features for chemicals, crystals, materials and biomolecules

Jmol is an interactive web browser applet.

This is a still image, but you can get an animated display of Jmol abilities by clicking here.

(The applet may take some seconds to load. Please, wait and do not reload the page in the meantime.)

The latest stable version is Jmol 12.2

EXTRACT RELEVANT INFORMATION:

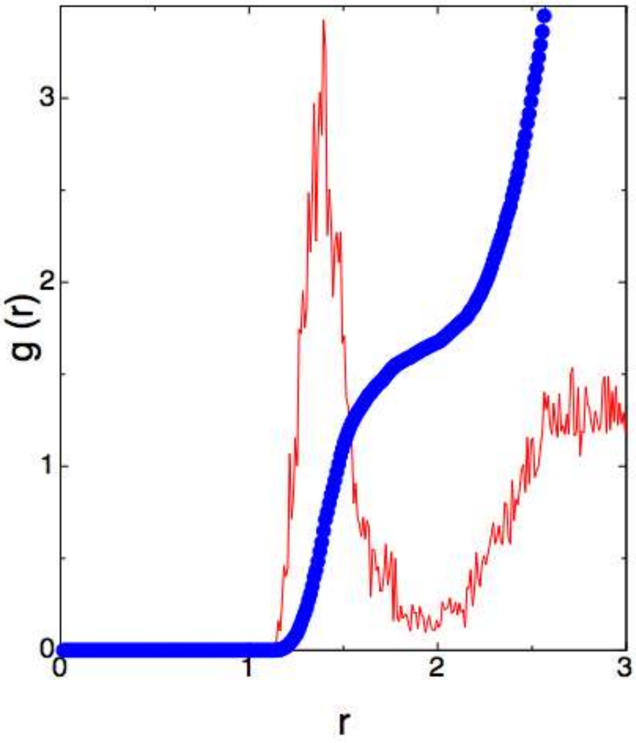
Atomic positions
Atomic velocities
Energy
Stress tensor

VISUALIZE SIMULATION (ex: jmol, vmd)

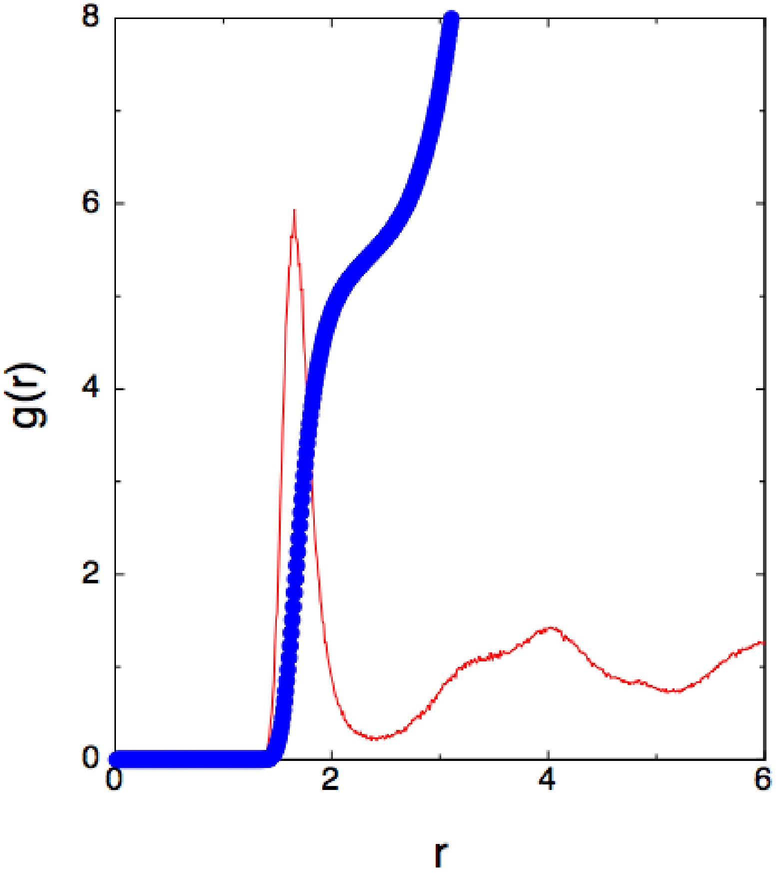
PERFORM STATISTICS

Ex: coordination in forsteritic melt at mid-mantle conditions

C-O



Si-O



Design of Catalysts and Electrocatalysts: From DFT Prediction to Experimental Verification

Jingguang Chen

Columbia University & BNL

Email: jgchen@columbia.edu

CFN Workshop, Nov. 5, 2014

Development of Novel Catalysts

- Supported catalysts:

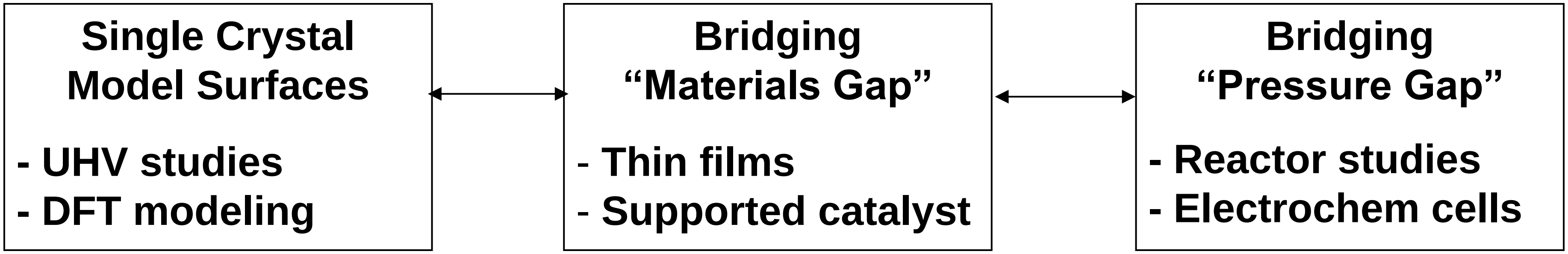
  - More relevant to commercial catalysts and processes
  - Fast (high throughput) evaluation
  - “Heterogeneous” in electronic and catalytic properties

- Single crystal surfaces:

  - Atomic level understanding from experiments and theory
  - Materials gap: single crystal vs. polycrystalline materials
  - Pressure gap: ultrahigh vacuum (UHV: ~10^{-12} psi)

- Need to bridge “materials gap” and “pressure gap”

From DFT Prediction to Experimental Verification



Single Crystal Model Surfaces

- **UHV studies**
- **DFT modeling**

Bridging “Materials Gap”

- **Thin films**
- **Supported catalyst**

Bridging “Pressure Gap”

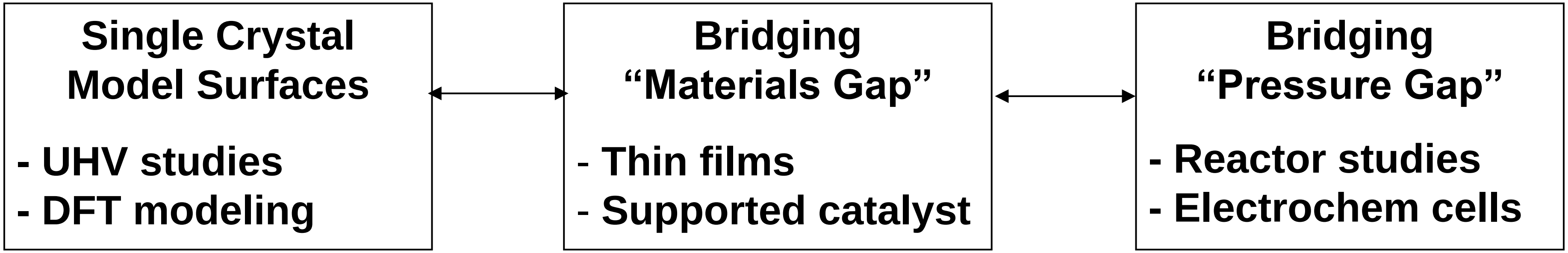
- **Reactor studies**
- **Electrochem cells**

Use DFT to assist catalysts design: (activity, selectivity, stability, cost):

- Binding energy calculations (activity, stability)

- Activation barriers and reaction network (selectivity)

Outline of Presentation



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Bridging “Materials Gap”

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Bridging “Pressure Gap”

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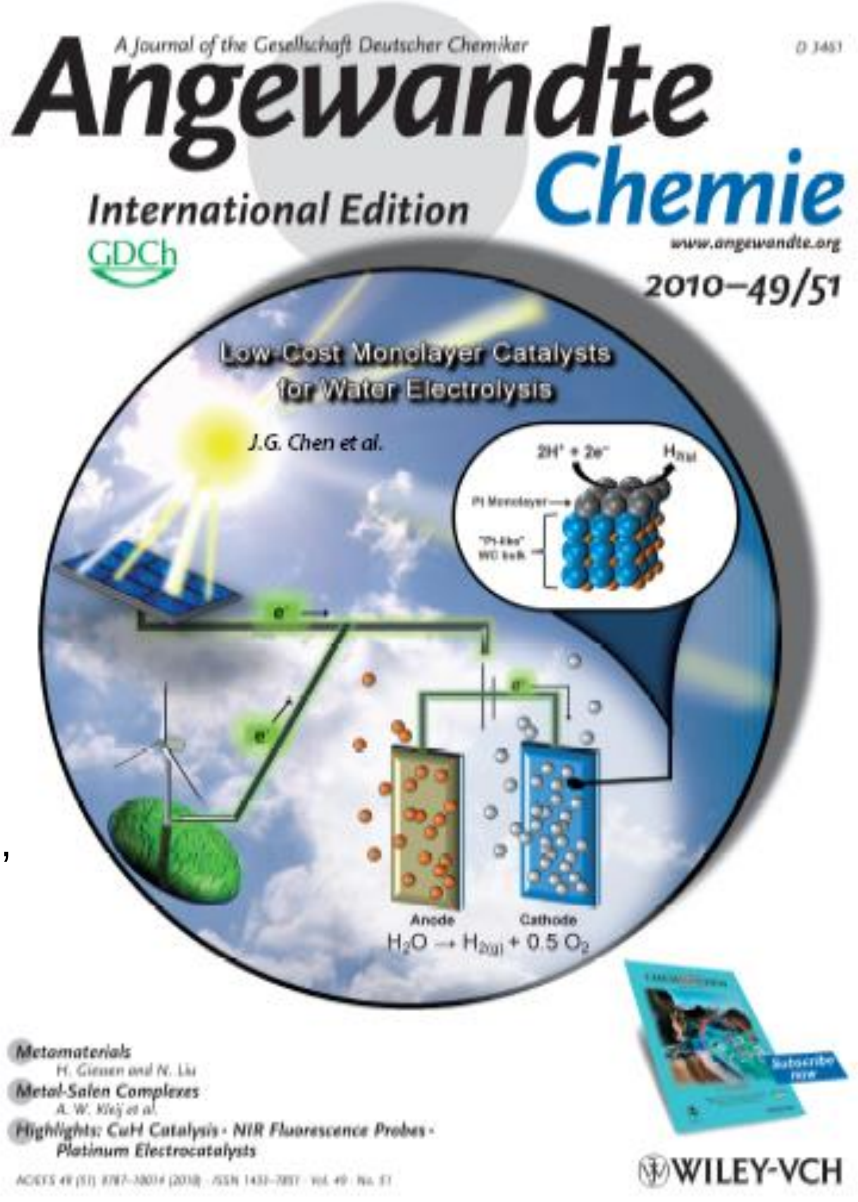
***Examples* of DFT prediction and experimental verification:**

- Correlating hydrogen binding energy (HBE) with water electrolysis activity
- Correlating hydrogen binding energy (HBE) with hydrogenation activity
- Correlating activation barrier with hydrogenation selectivity

Correlating HBE with Water Electrolysis Activity



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

GDCh

www.angewandte.org

2010–49/51

Low-Cost Monolayer Catalysts for Water Electrolysis

J.G. Chen et al.

Metamaterials
H. Giessen and N. Liu

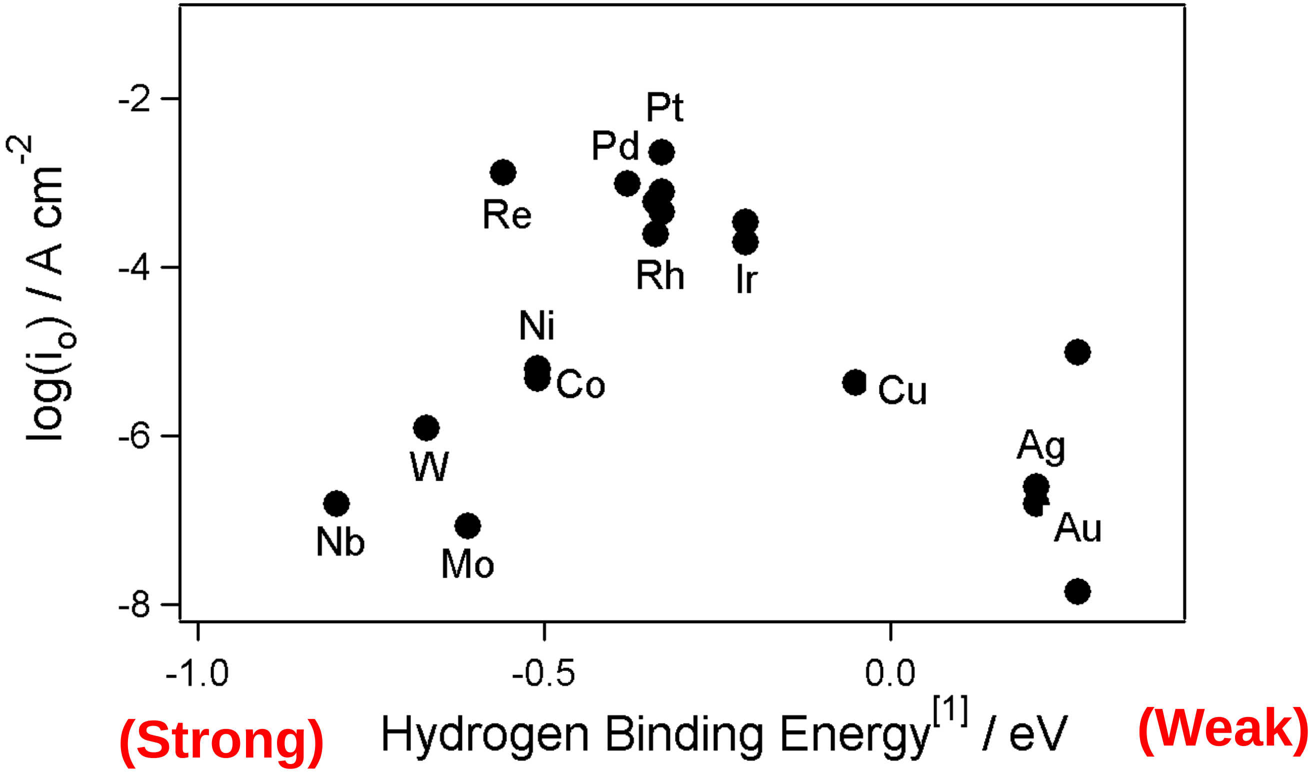
Metal-Salen Complexes
A. W. Kleij et al.

Highlights: *CuH Catalysis · NIR Fluorescence Probes · Platinum Electrocatalysts*

WILEY-VCH

Esposito, Hunt & Chen,
Angew. Chem. Int. Ed.
49 (2010) 9859

HER Activity and Hydrogen Binding Energy (HBE)



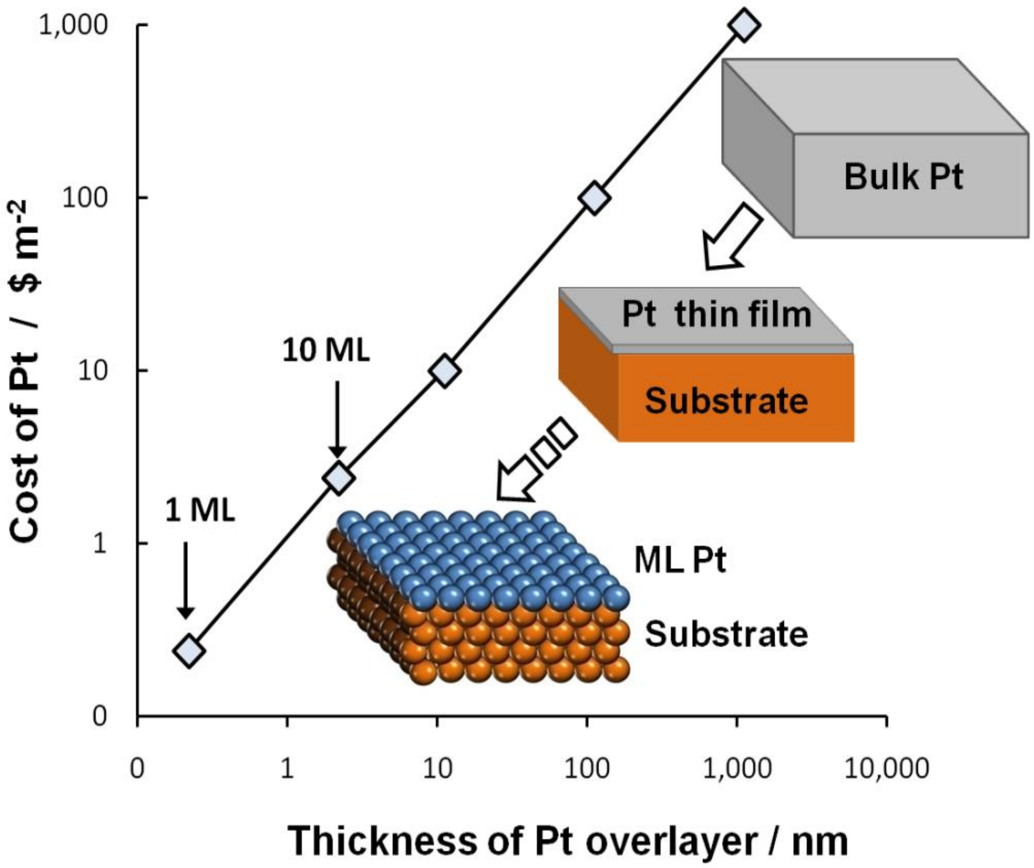
- Classic volcano curve observed for the HER is explained by Sabatier'sPrinciple

$$H^+ + e^- + * \rightarrow H^* \qquad \text{(Volmer Step)}$$

$$2H^* \rightarrow H_{2(g)} + 2* \qquad \text{(Tafel Step)}$$

[1] Data from: Norskov, Bligaard, Logadottir, Kitchin, Chen, Pandelov, Stimming, J.Electrochem. Soc., 152 (2005) J23-26.

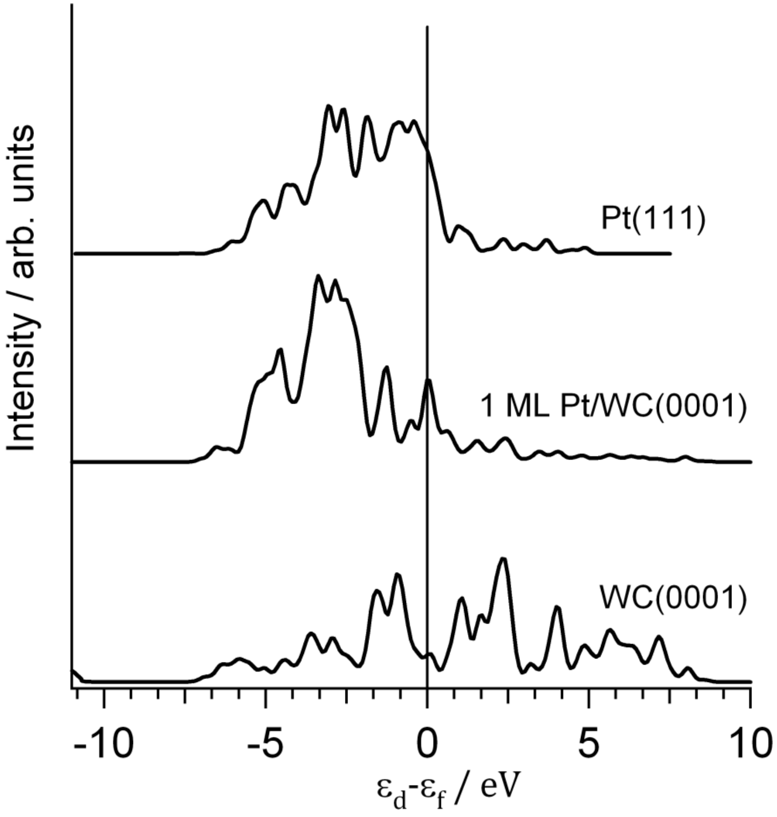
Reduce Pt Loading with Monolayer (ML) Pt



Goal: Supporting ML Pt on Pt-like substrates, such as WC

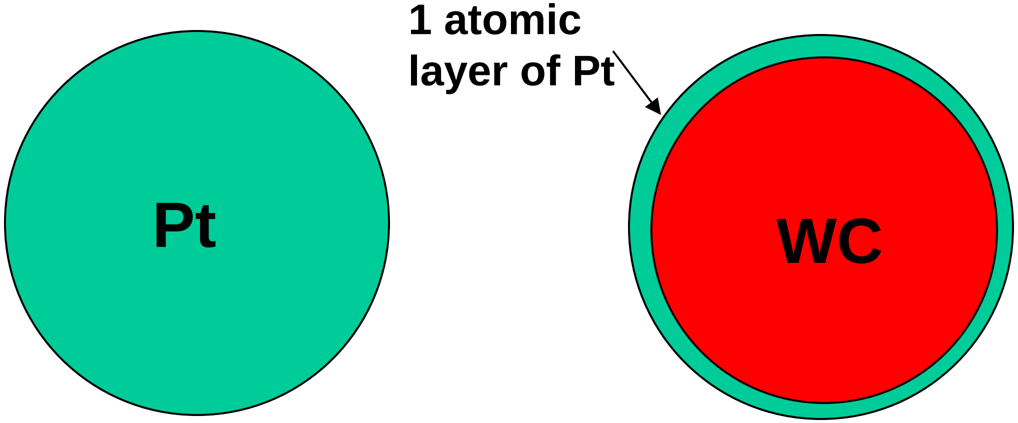
DFT Prediction: Similar HBE Values between Monolayer Pt-WC and Bulk Pt

d-band density of states

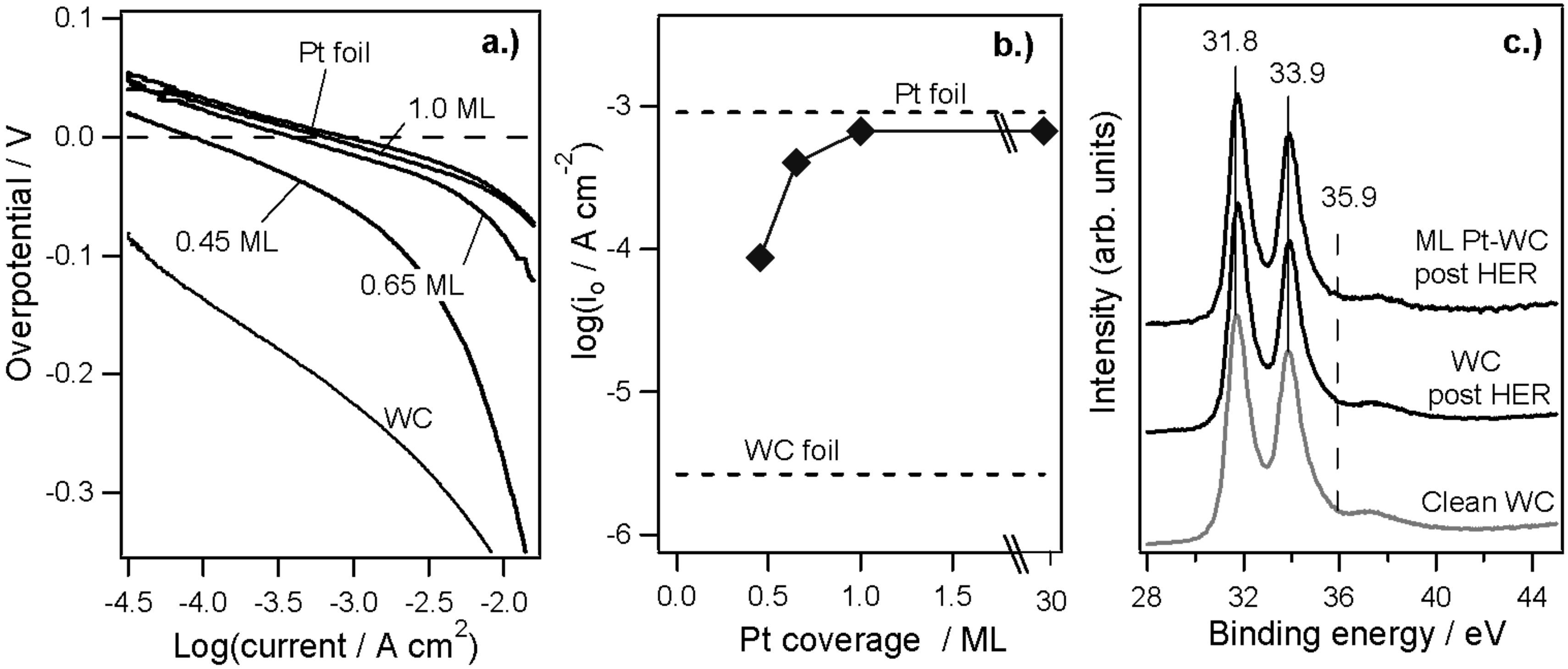


Surface	HBE (eV)
WC(001)	-0.99
Pt(111)	-0.46
1 ML Pt-WC(001)	-0.43

DFT-calculated per-atom hydrogen binding energy (HBE) for WC, Pt, and 1 ML Pt-WC surfaces with a hydrogen coverage of 1/9 ML.



Experimental Verification of Activity and Stability



HER Activity of 1 ML Pt/WC approaches to that of Pt foil

Esposito, Hunt, Birmire & Chen, *Angew. Chem. Int. Ed*. 49 (2010) 9859

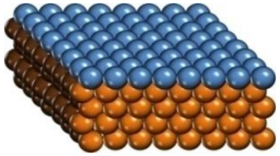
DFT Prediction of Stability of Pt/WC and Pt/C

- Use DFT to compare adhesion of Pt atoms to WC and Pt surfaces:

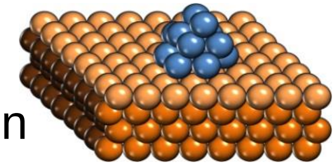
Binding Energy

Outcome

Pt-(Substrate) **<** Pt-Pt ⇨

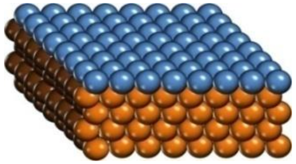


Pt → migration



Particles favored

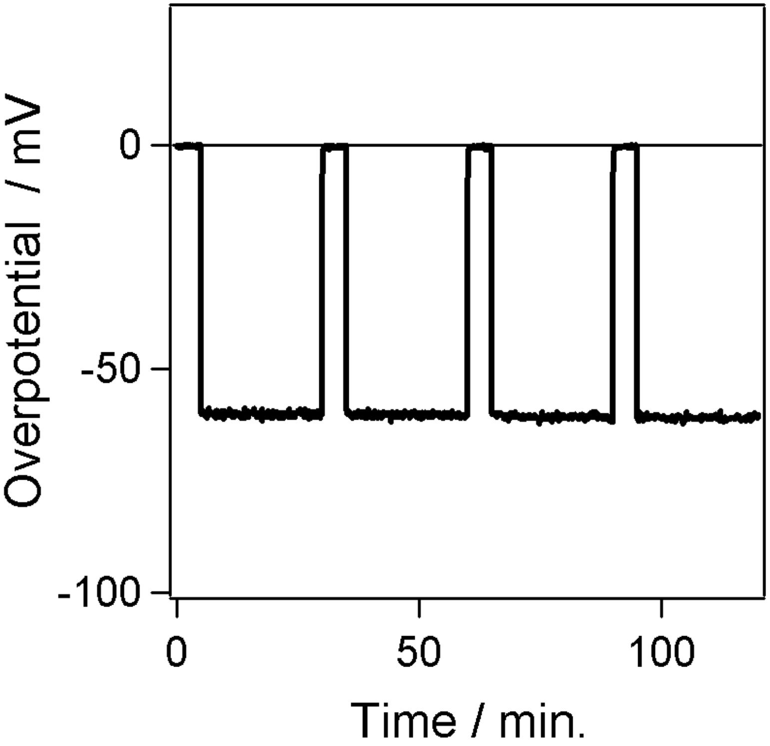
Pt-(Substrate) **>** Pt-Pt ⇨



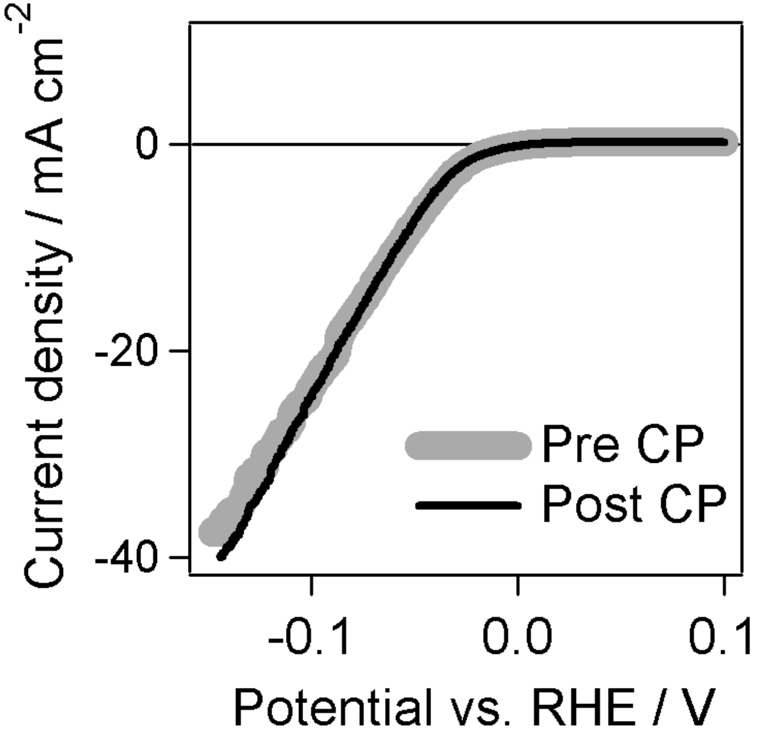
ML configuration favored

ML surface atoms	Substrate	Binding energy / eV	(M-X^) - (M-M) BE / eV
Pt	Pt(111)	-5.43	0.00
	C(0001)	-4.12	**1.31**
	WC(0001)	-6.59	**-1.16**
	W_2C(0001)	-6.51	-1.08

Experimental Verification of HER Stability



Chronopotentiometry

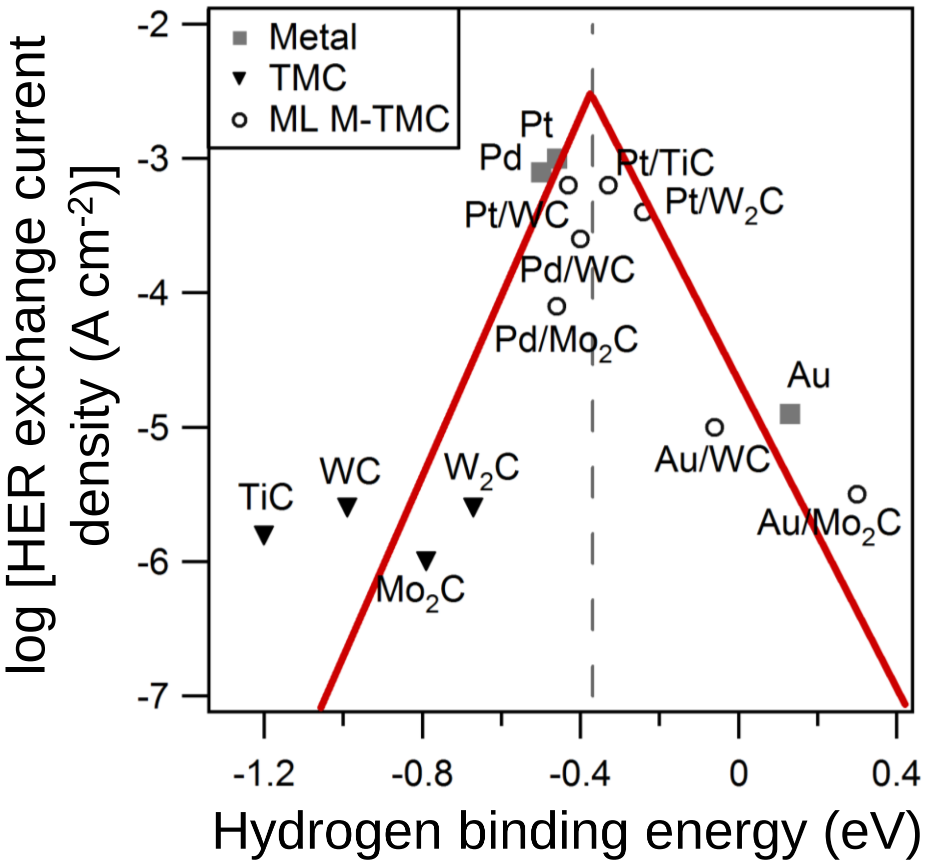


Linear Sweep Voltammetry

- No change in overpotential observed with time
- No change in LSV before and after CP
- XPS and SEM measurements confirmed stability

Esposito, Hunt & Chen, *J. Am. Chem. Soc.* 134 (2012) 3025

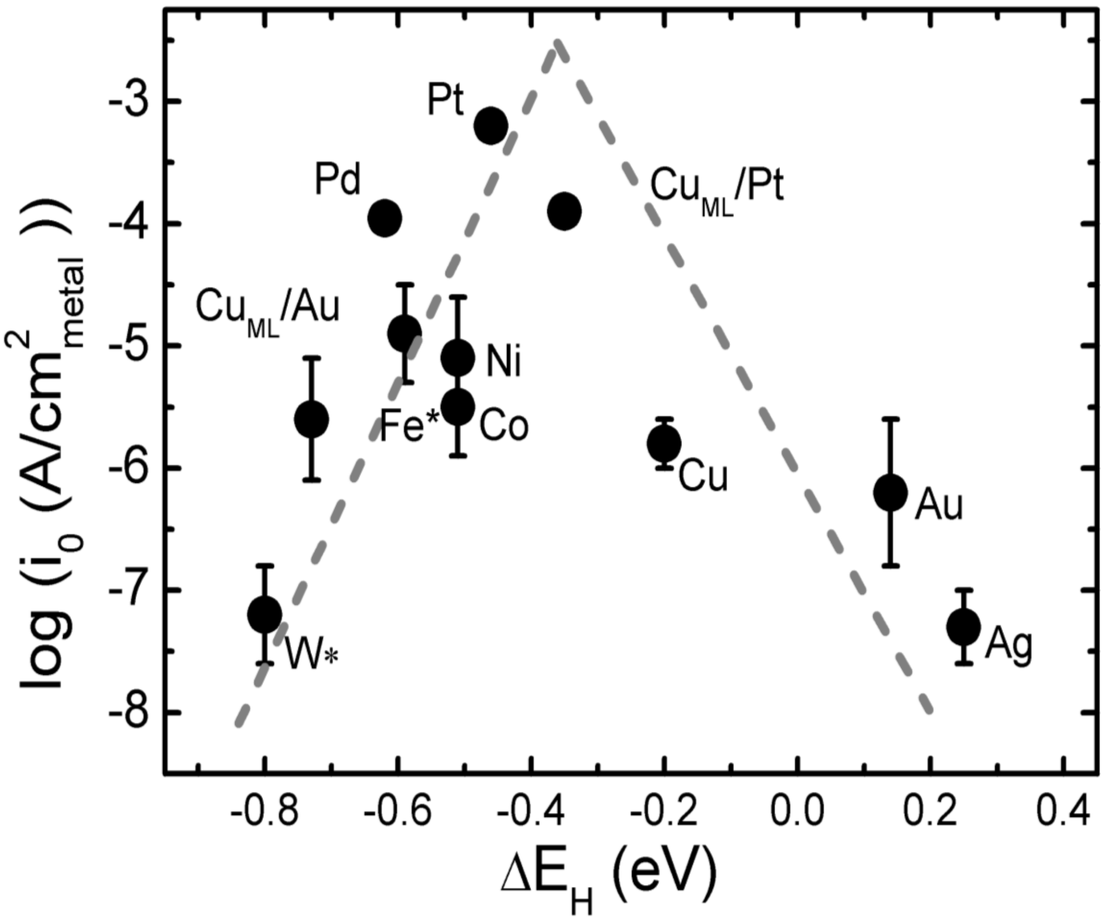
Other ML/TMC Electrocatalysts for HER in Acid



Volcano relationship provides design principles of electrocatalysts

Kimmel , Yang & Chen, *J. Catalysis, 312 (2014) 216*

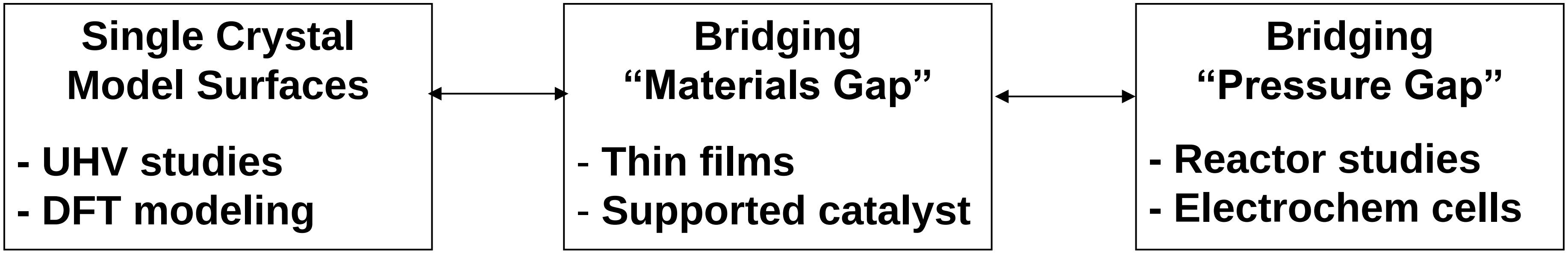
HER Catalysts in Alkaline Environment



Volcano relationship also appears to hold in alkaline electrolyte

Sheng et al. *Energy & Env. Sci*. 6 (2013) 1509

Outline of Presentation



Single Crystal Model Surfaces

- **UHV studies**
- **DFT modeling**

Bridging "Materials Gap"

- **Thin films**
- **Supported catalyst**

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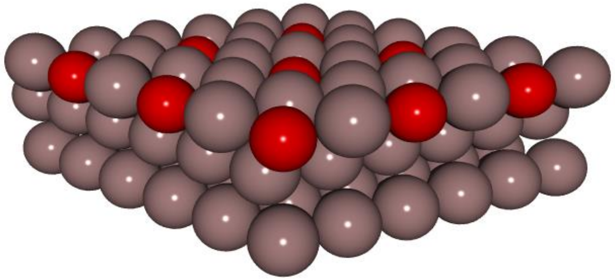
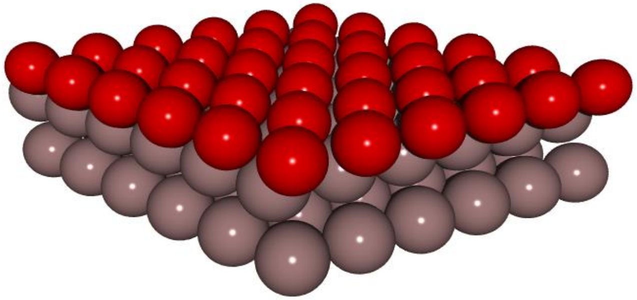
***Examples* of DFT prediction and experimental verification:**

- Correlating hydrogen binding energy (HBE) with water electrolysis activity
- Correlating hydrogen binding energy (HBE) with hydrogenation activity
- Correlating activation barrier with hydrogenation selectivity

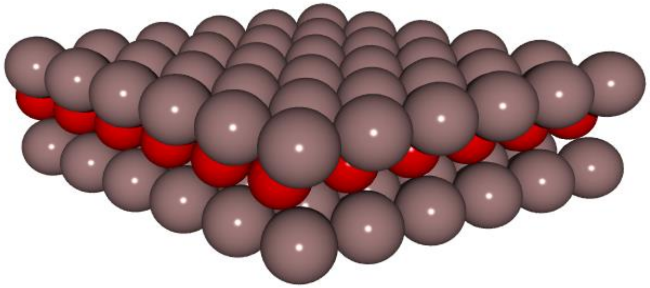
Monolayer Bimetallic Surfaces

Surface Alloy





Surface Monolayer

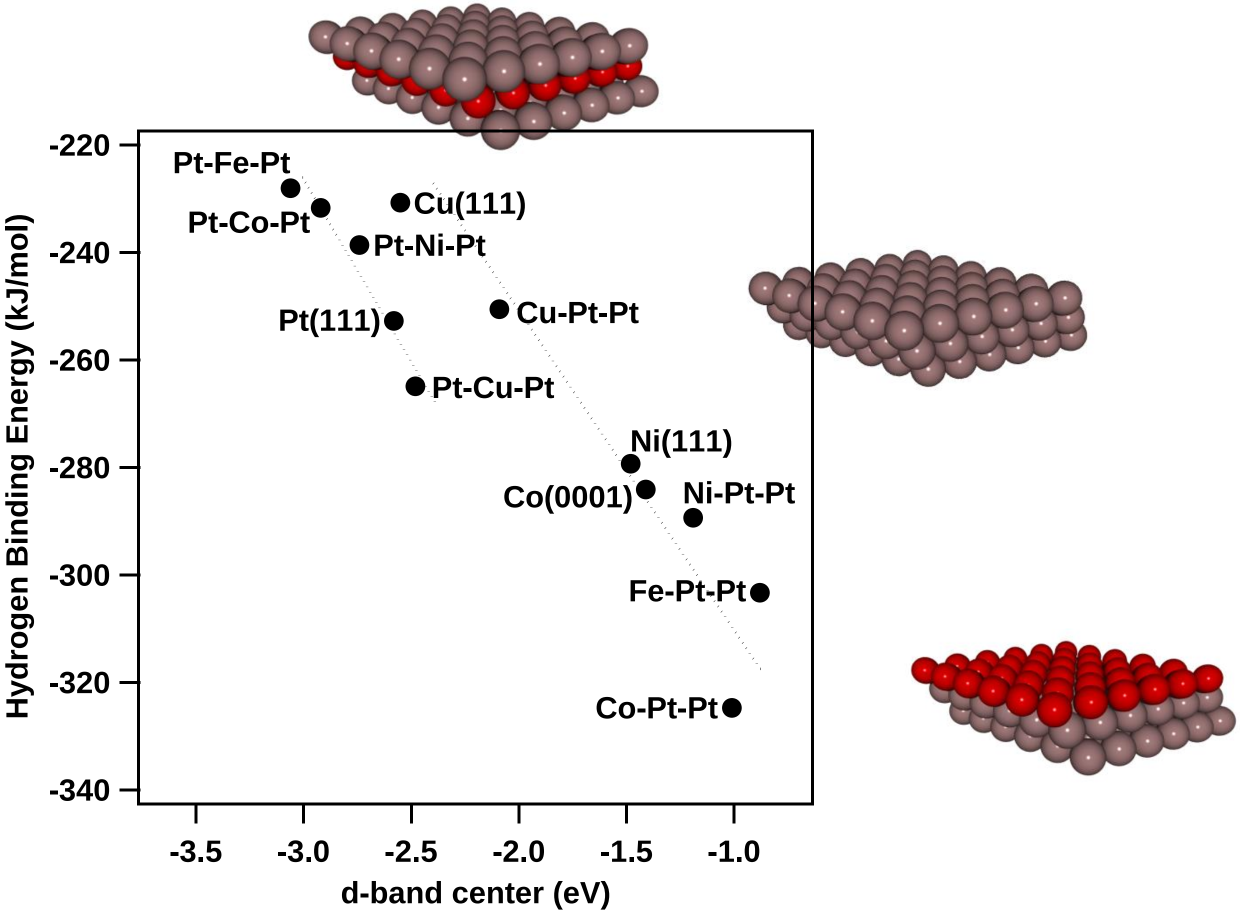


Subsurface Monolayer

Modified surface chemical properties due to:

- –Ligand effect – electronic configuration
- –Compressive and tensile strain - lattice mismatch

DFT Prediction of HBE Values



Hydrogen binding energy (HBE) can be controlled by surface structures

Kitchin, Norskov, Barteau & Chen, *Phys. Rev. Lett*. 93 (2004) 156801
Murillo, Goda & Chen, *J. Am. Chem. Soc.* 129 (2007) 7101

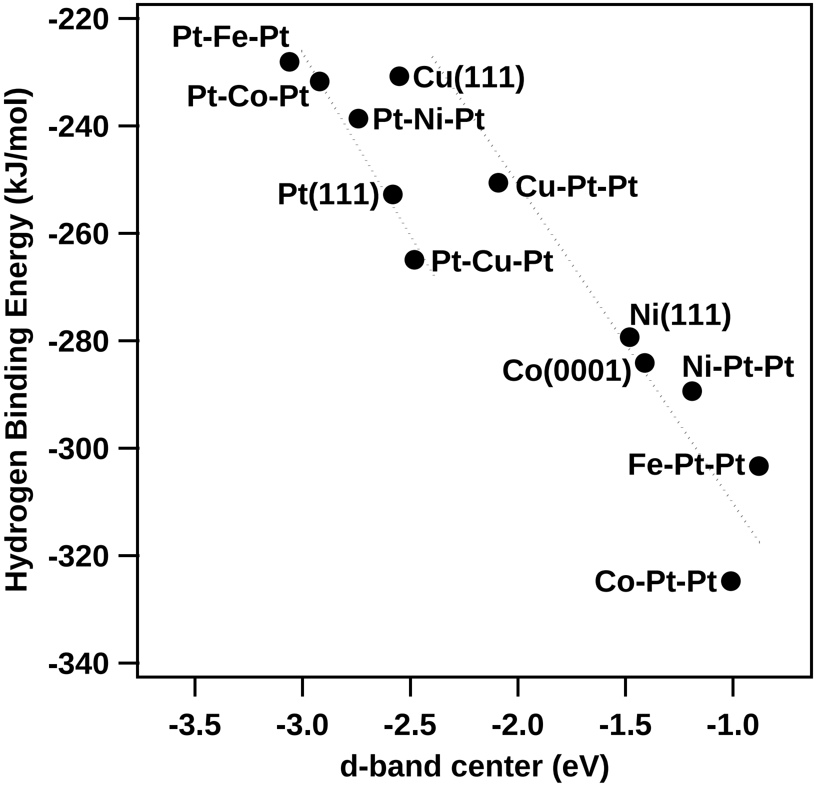
Controlling Hydrogenation Activity:
Correlating with Binding Energy

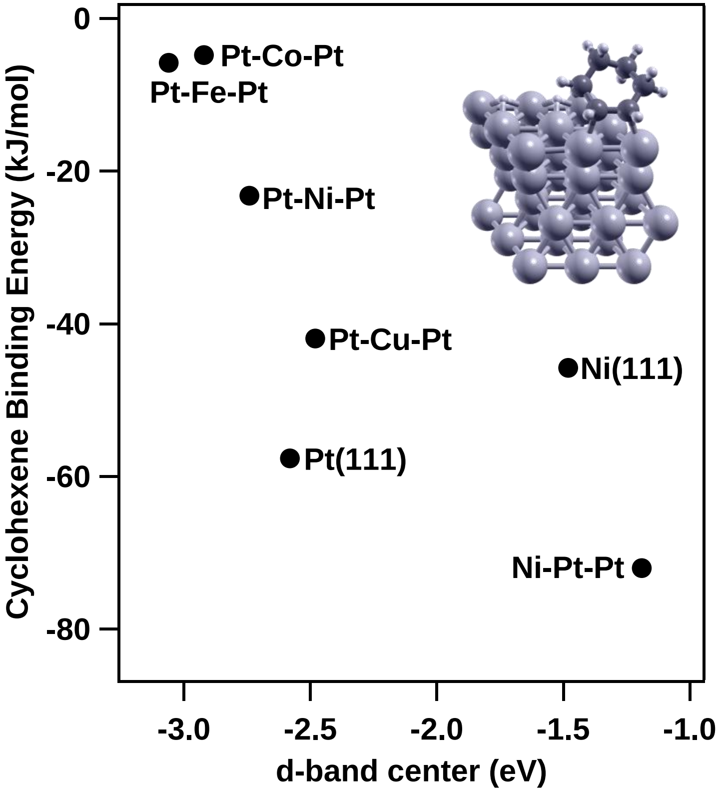
Low-Temperature Cyclohexene Hydrogenation:

Assumption for Higher Hydrogenation Activity:

- Weakly bonded H atoms
- Weakly bonded cyclohexene

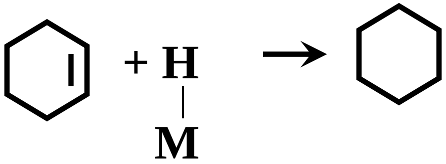
DFT Calculations of Binding Energies of Hydrogen and Cyclohexene

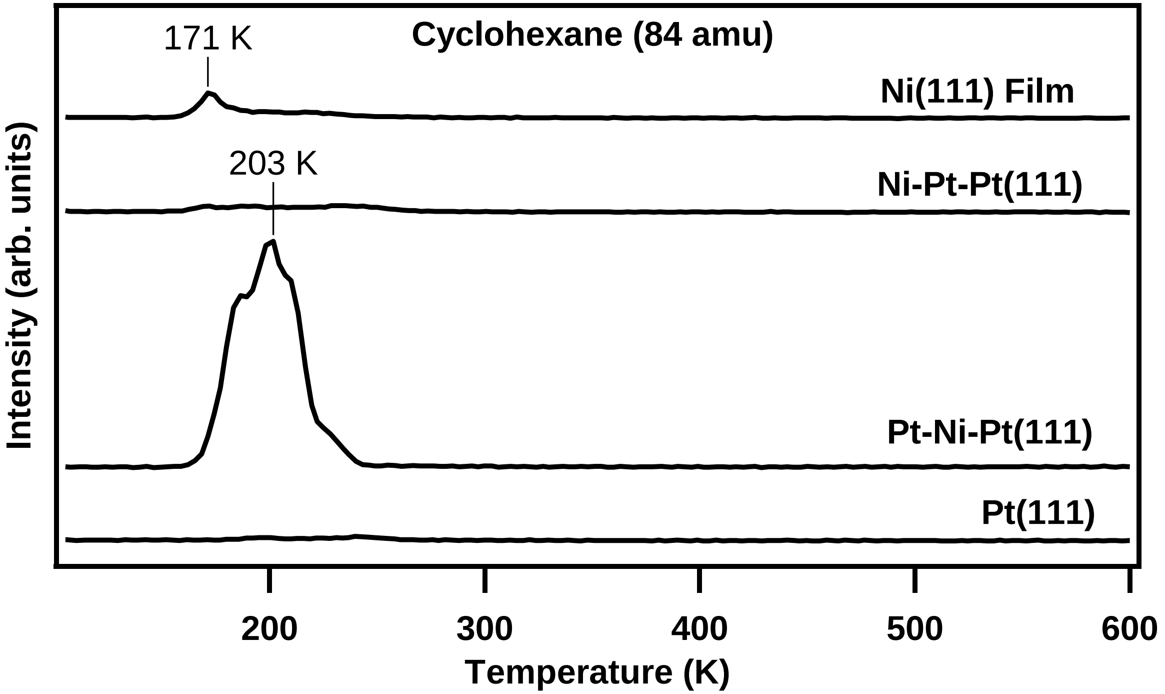


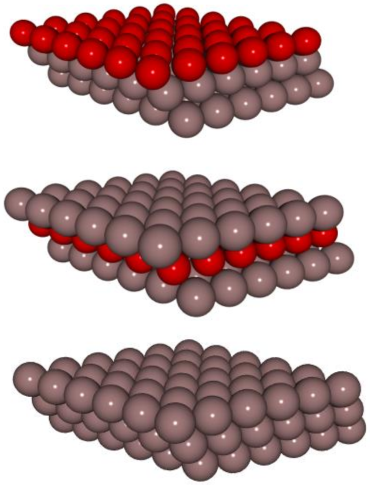


BE values follow the same trend: Ni-Pt(111) > Ni ~ Pt > Pt-Ni-Pt(111)

Low-Temperature Hydrogenation of Cyclohexene Due to Weakly Bonded H

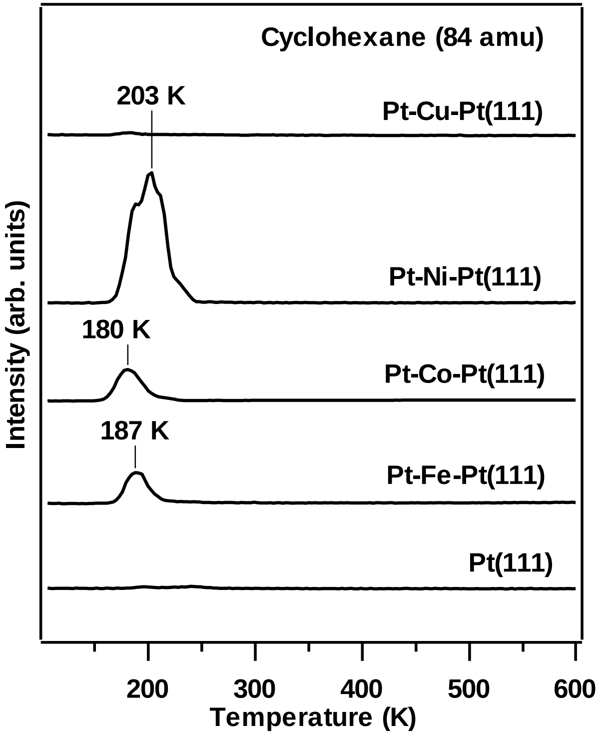


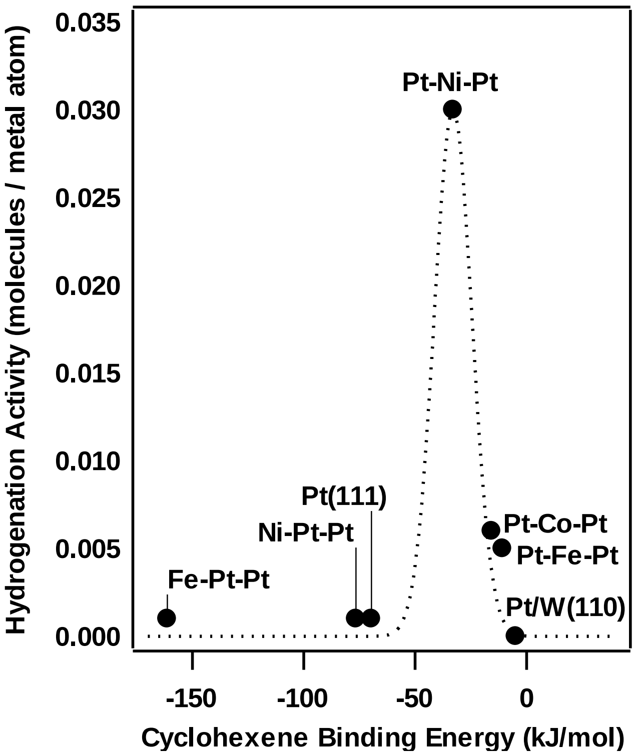




- Weakly bonded M-H leads to low-T hydrogenation

Binding Energies Correlate with Cyclohexene Hydrogenation Activity





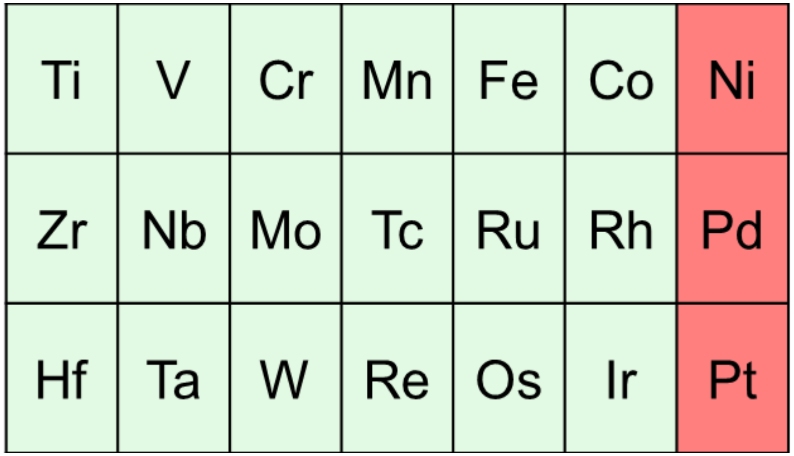
Sabatier’s principle: not too strong, not too weak!

Volcano relationship allows prediction of hydrogenation activity

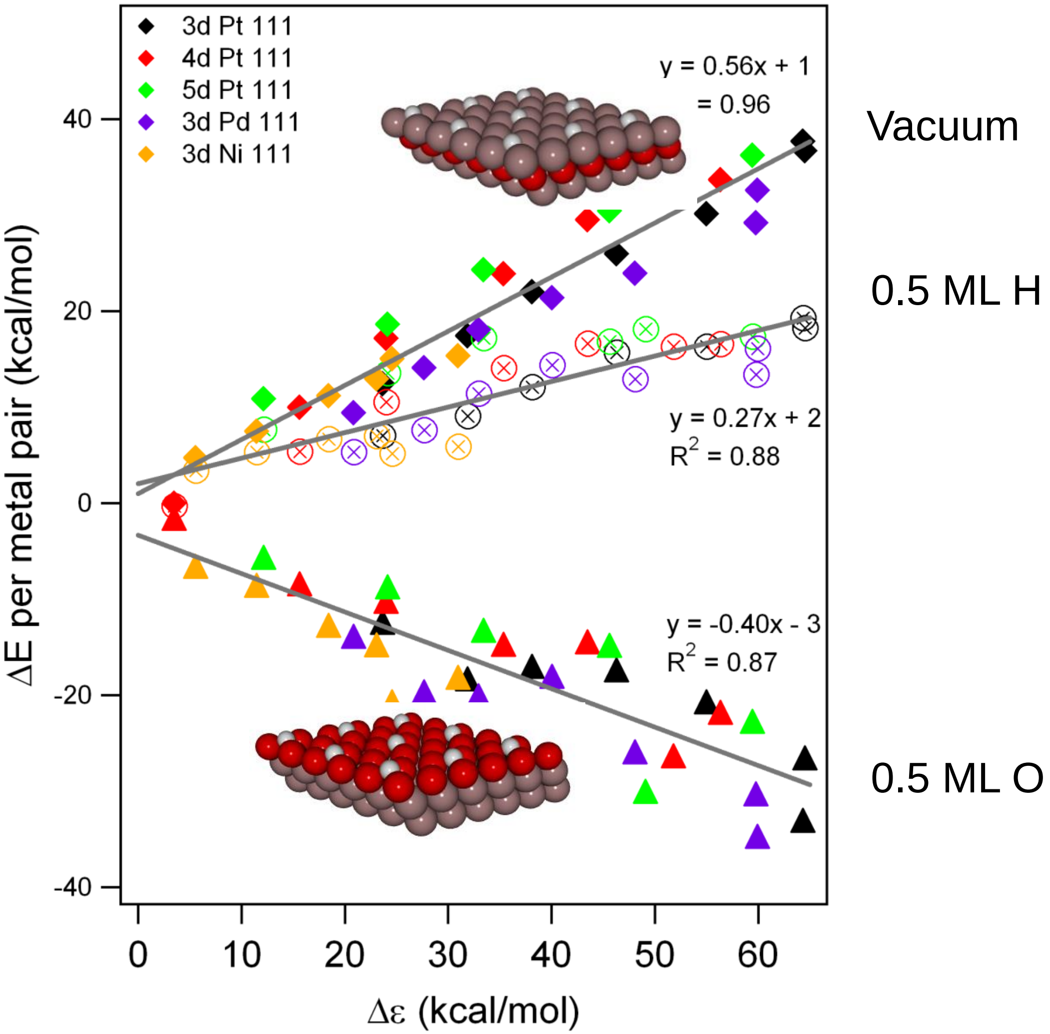
DFT Prediction of Stable Bimetallic Structures

General Stability includes:

- Admetals – 3d, 4d, 5d
- Host metals – Ni, Pd, Pt



Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

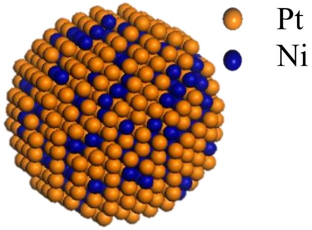


Menning & Chen,

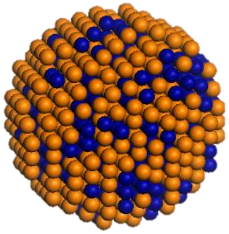
J. Chem. Phys, 130 (2009) 174709

Experimental Verification of Bimetallic Structures

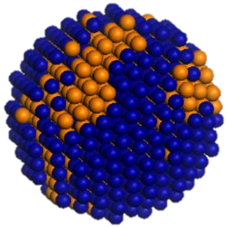
Coordination Number	***10% H_2 at 50 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	1.9 ± 0.8	2.696 ± 0.003
Pt-Ni	3.5 ± 0.4	3.904 ± 0.007



Coordination Number	***10% H_2 at 225 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	2.0 ± 0.7	2.675 ± 0.005
Pt-Ni	3.8 ± 0.3	4.148 ± 0.008

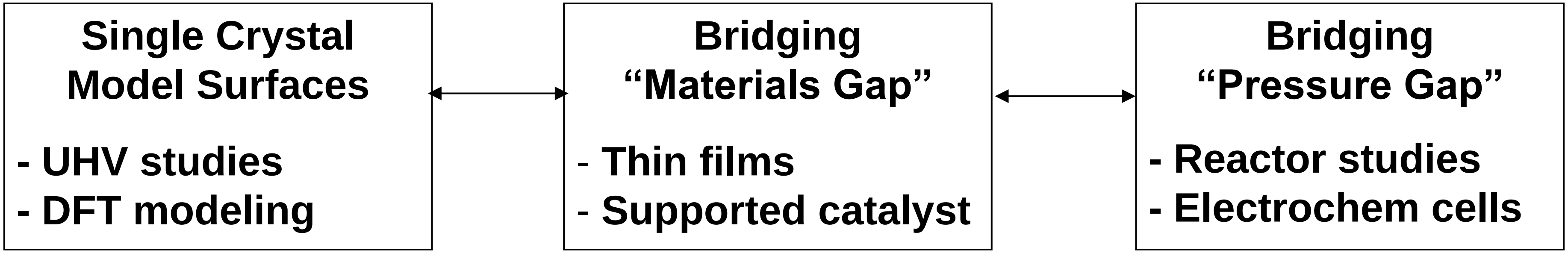


Coordination Number	***APR at 225 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	6.0 ± 1.4	4.429 ± 0.006
Pt-Ni	1.9 ± 0.8	2.24 ± 0.03



Tupy, Karim, Vlachos, Chen, *ACS Catal*ysis, 2 (2012) 2290

Outline of Presentation



Single Crystal Model Surfaces

- UHV studies
- DFT modeling

Bridging "Materials Gap"

- Thin films
- Supported catalyst

Bridging "Pressure Gap"

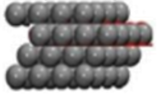
- Reactor studies
- Electrochem cells

***Examples* of DFT prediction and experimental verification:**

- Correlating hydrogen binding energy (HBE) with water electrolysis activity
- Correlating hydrogen binding energy (HBE) with hydrogenation activity
- Correlating activation barrier with hydrogenation selectivity

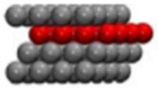
Selective Hydrogenation Requires More Complicated DFT Calculations

Activation barriers on Pd(111) surface (eV):


Pd(111)

$$C_4H_6 \underset{\text{-H } 0.64}{\overset{\text{+H } 1.04}{\rightleftarrows}} C_4H_7 \underset{\text{-H } 0.49}{\overset{\text{+H } 0.92}{\rightleftarrows}} C_4H_8 \underset{\text{-H } 0.49}{\overset{\text{+H } 1.01}{\rightleftarrows}} C_4H_9 \underset{\text{-H } 1.05}{\overset{\text{+H } 0.87}{\rightleftarrows}} C_4H_{10}$$

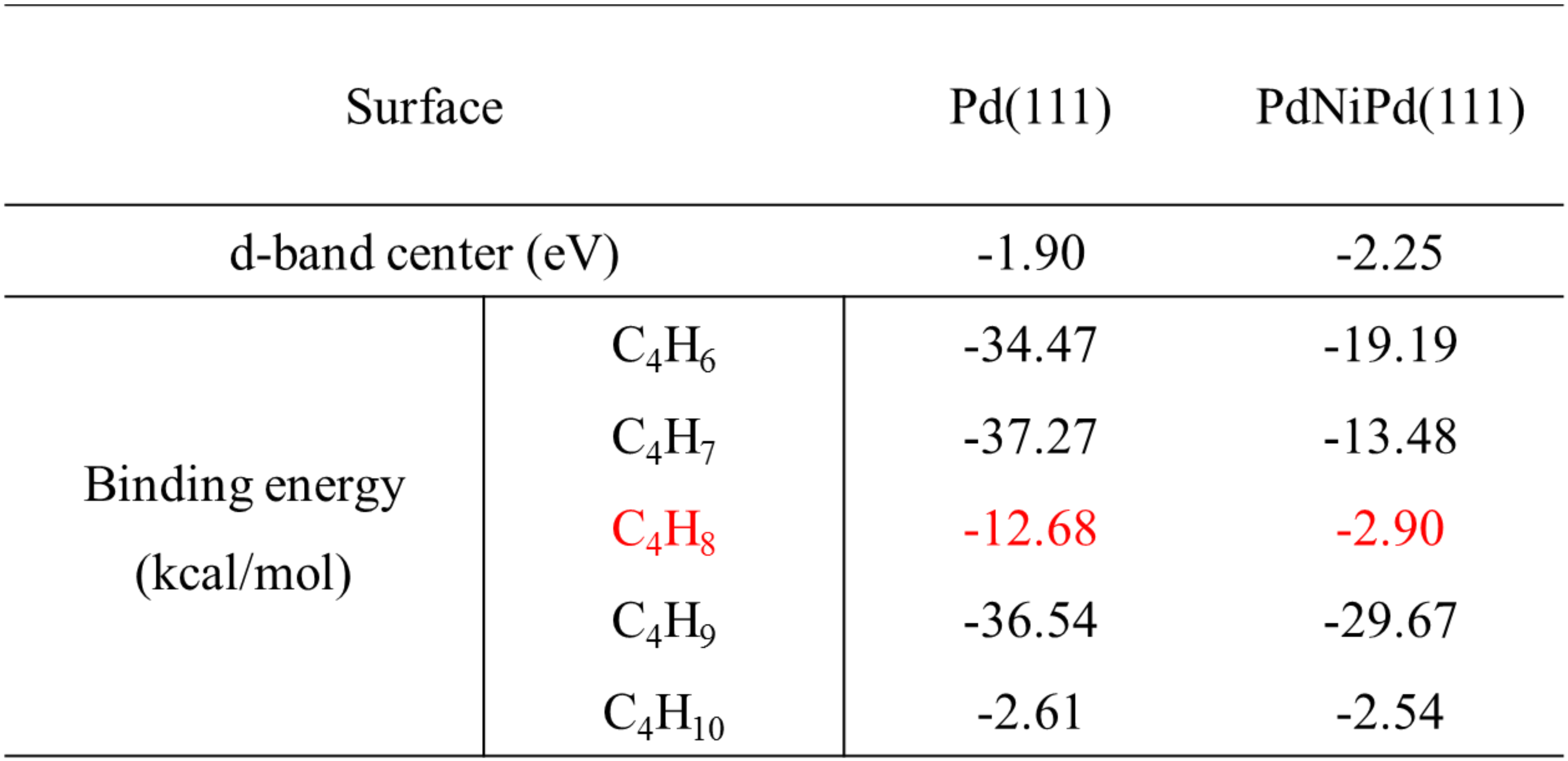
Activation barriers on PdNiPd(111) surface (eV):


PdNiPd(111)

$$C_4H_6 \underset{\text{-H } 0.60}{\overset{\text{+H } 0.68}{\rightleftarrows}} C_4H_7 \underset{\text{-H } 1.03}{\overset{\text{+H } 0.88}{\rightleftarrows}} C_4H_8 \underset{\text{-H } 0.81}{\overset{\text{+H } 0.88}{\rightleftarrows}} C_4H_9 \underset{\text{-H } 1.52}{\overset{\text{+H } 0.80}{\rightleftarrows}} C_4H_{10}$$

The activation barriers are generally lower on PdNiPd(111) than on Pd(111), leading to higher hydrogenation activity on PdNiPd(111)

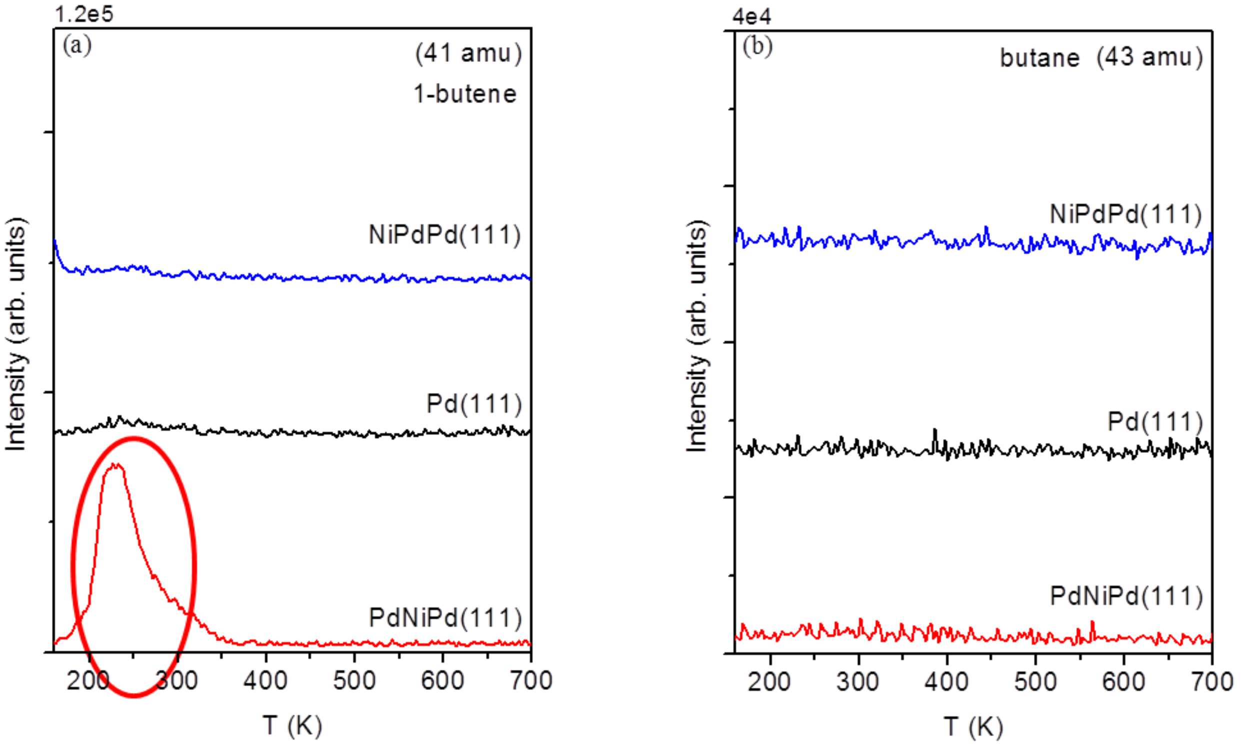
Predicting Selectivity Requires DFT Calculations of Reaction Network



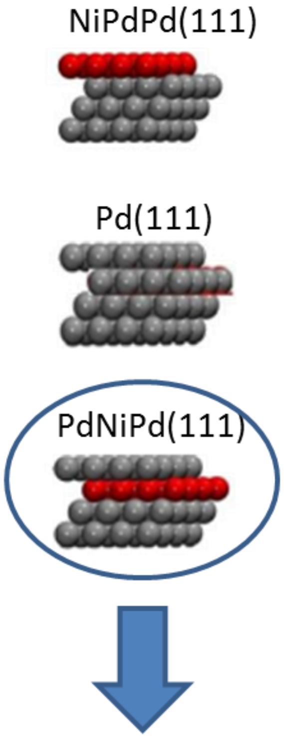
Surface		Pd(111)	PdNiPd(111)
d-band center (eV)		-1.90	-2.25
Binding energy (kcal/mol)	C_4H_6	-34.47	-19.19
	C_4H_7	-37.27	-13.48
	C_4H_8	-12.68	-2.90
	C_4H_9	-36.54	-29.67
	C_4H_{10}	-2.61	-2.54

Binding energy of butene is weaker on PdNiPd(111), leading to higher selectivity for butene production on PdNiPd(111)

Experimental Verification on Model Surfaces



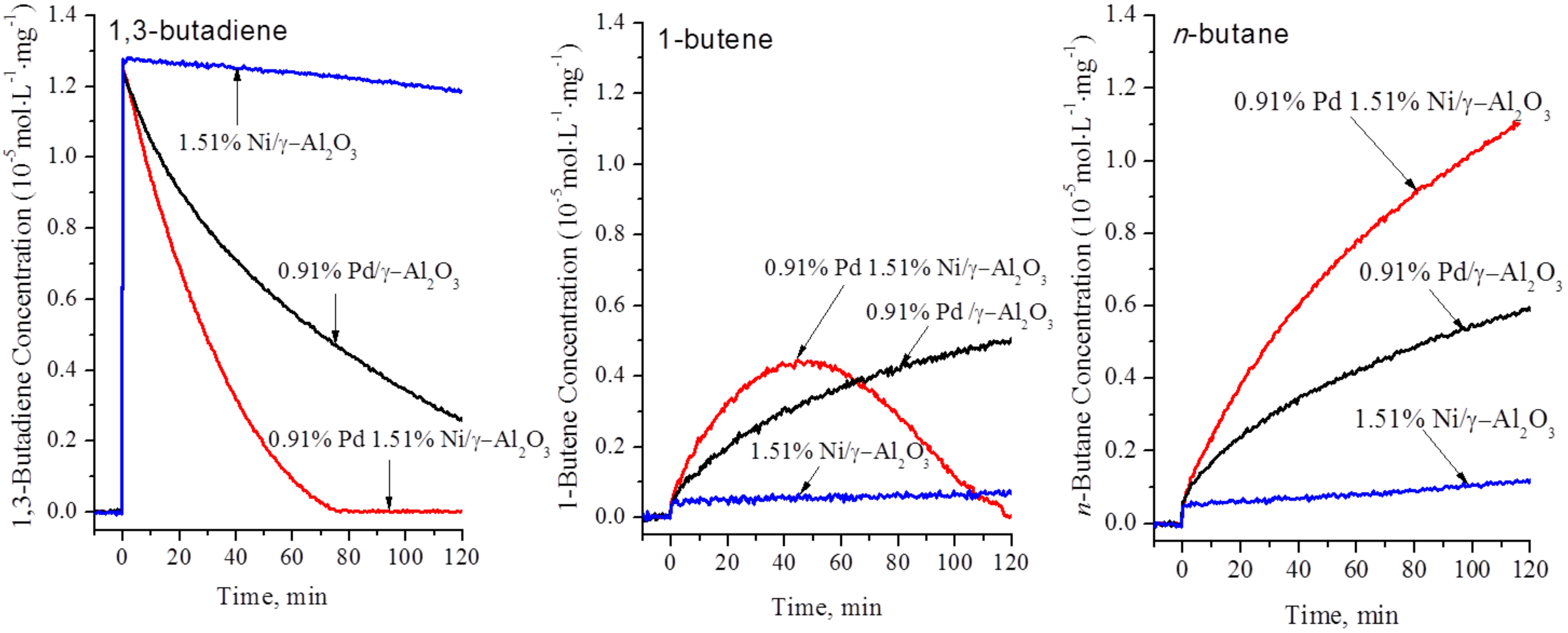
UHV-TPD: Ultra-High Vacuum Temperature Programmed Desorption



Stable bimetallic structure
under hydrogenation conditions

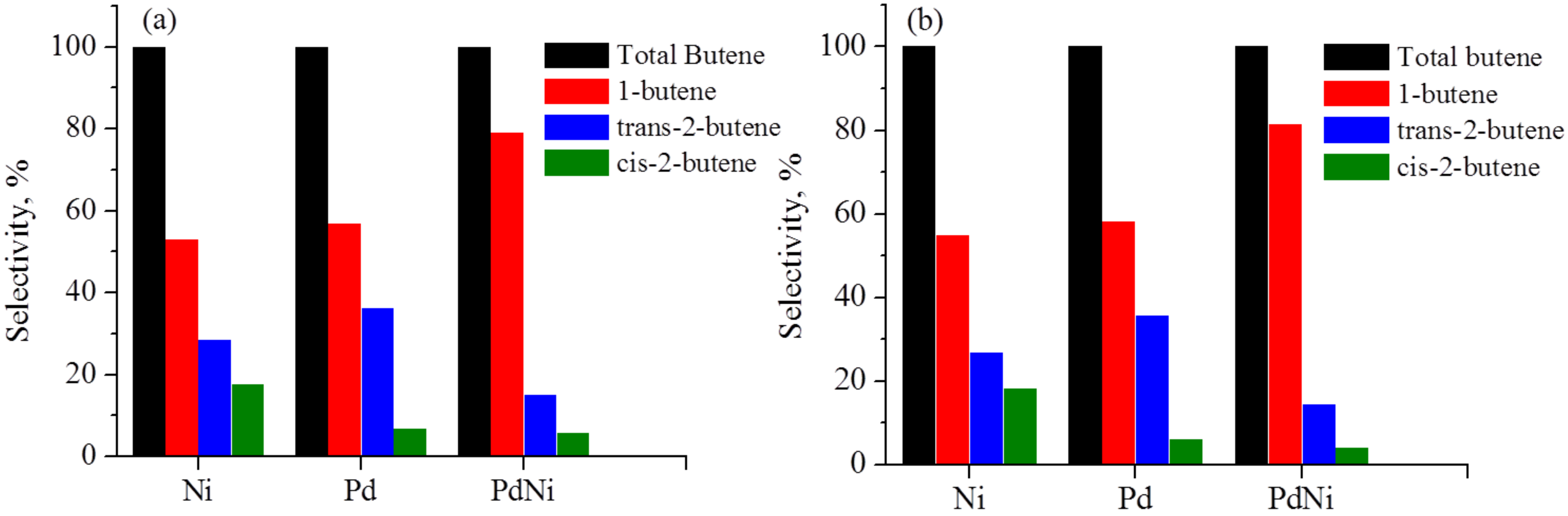
PdNiPd bimetallic structure is very active for 1,3-butadiene hydrogenation, and may also be selective for 1-butene production

Batch Reactor: Hydrogenation Activity



Activity trend: PdNi > Pd >> Ni

Flow Reactor: Hydrogenation Selectivity



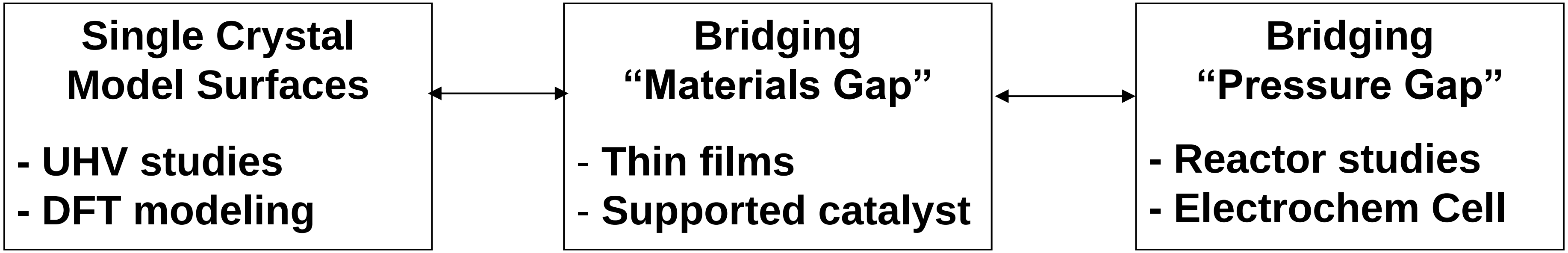
Selectivities in flow reactor at conversions of (a) 10% (b) 60%
H_2:C_4H_6 = 2.2:1 Total Flow Rate: 9.6 ml/min

PdNi shows higher 1-butene selectivity than Pd, and higher yield in producing 1-butene

Hou, Porosoff, Chen & Wang, *J. Catalysis*, 316 (2014) 1

Conclusions

- Bimetallic and carbide catalysts offer the advantages of reduced cost and enhanced activity, selectivity and stability
- Combined theory, surface science, and catalytic studies are critical in design of novel catalytic materials



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Review: Yu, Porosoff & Chen, “Review of Pt-based Bimetallic Catalysis: From Model Surfaces to Supported Catalysts”, *Chemical Reviews*, 112 (2012) 5780