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AB-INTIO ELECTRONIC STRUCTURE CALCULATIONS - II

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Local Density and Local Spin Density approx.

To make Kohn-Sham eqs. of practical use we must give a practical recipe to calculate, in an approximate way, the Exc functional.

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_0(r)\, n(r)\, d^3r + V_{nn}$$

$$V_{KS}(r) = V_0(r) + e^2 \int \frac{n(r')}{|r-r'|}\, d^3r' + v_{xc}(r) \; ; \qquad v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right] \varphi_i(r) = \varepsilon_i\, \varphi_i(r)$$

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

Already Kohn and Sham in their original 1965 paper proposed the simplest one: the Local Density Approximation, widely used since then. Actually, LDA, with its spin-polarized version LSD, has been the only very successful scheme considered in applications up to recent times.

LDA, based on the local nature of xc, gives Exc as

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

where $\varepsilon_{xc}^{hom}(n)$ is the xc energy per particle of the homogeneous electron-gas with density n. According to LDA each elemental volume contributes to the total Exc as it would in an homogeneous system with the same density.
Note that $\varepsilon_{xc}^{hom}(n)$ is an ordinary function of the (local) density and that it is a KNOWN function).

$$\mathcal{E}_{xc}^{hom}(n) = \mathcal{E}_x^{hom}(n) + \varepsilon_c^{hom}(n)$$

$$\mathcal{E}_x^{hom}(n) = -\frac{3}{4\pi} e^2 \left(3\pi^2 n\right)^{1/3}$$ can be computed analytically within HF

$\varepsilon_c^{hom}(n)$ has been accurately determined by DMC technique by D. Ceperley and B. J. Alder, Phys. Rev. Lett. 45 566 (1980). There are NO free parameter to adjust.

Several forms for $\varepsilon_{xc}^{hom}(n)$ were proposed before CA calculation but there is no reason not to use the best values now available (CA in the PZ or VWN parametric form), but because other less accurate forms are occasionally closer to experiment... but this is not serious.

Within LDA the xc potential is simply

$$v_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} = \left.\frac{d\left(n\,\varepsilon_{xc}^{hom}(n)\right)}{dn}\right|_{n=n(r)}$$

There is instead some freedom we can exploit in the choice of the auxiliary KS system.
All the necessary information is contained in $F[n]$ but in magnetic systems or, in general, in systems where open shells are involved it may be more useful (leads to more realistic approximate functionals) to write things in terms of $(n_\uparrow(r), n_\downarrow(r))$ allowing the system to behave differently according to the spin

$$F[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, n_\downarrow] + E_H[n_\uparrow + n_\downarrow] + E_{xc}[n_\uparrow, n_\downarrow]$$

As far as the auxiliary KS system is concerned the two spin subspaces are two separated world each with its own effective potential to be determined self-consistently

Kohn-Sham eqs read:

$$V^{\uparrow}_{KS}(r) = V_0(r) + V_H(r) + \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\uparrow(r)}$$

$$V^{\downarrow}_{KS}(r) = V_0(r) + V_H(r) + \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\downarrow(r)}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{\sigma}_{KS}(r)\right]\varphi^{\sigma}_i(r) = \varepsilon^{\sigma}_i\,\varphi_i(r) \qquad \sigma = \uparrow,\downarrow$$

$$n_\sigma(r) = \sum_{\varepsilon^{\sigma}_i < \varepsilon_F} |\varphi^{\sigma}_i(r)|^2$$

and ε_F is determined by the condition on the total number of electrons.

Within Local Spin Density approx $E_{xc}[n_\uparrow, n_\downarrow]$ is approximated by

$$E^{LSD}_{xc}[n_\uparrow, n_\downarrow] = \int \left(n_\uparrow(r) + n_\downarrow(r)\right)\varepsilon^{hom}_{xc}(n_\uparrow(r), n_\downarrow(r))\, d^3r$$

where $\varepsilon^{hom}_{xc}(n_\uparrow, n_\downarrow)$ is also a KNOWN function (again from CA)

For non magnetic systems LSD reduces to LDA. So if you know your system is spin unpolarized you can spare half of the calculation time using LDA.

More on LDA-LSD

O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B 13, 4274 (1976)

R.O. Jones and O. Gunnarsson, Rev. Mod. Phys 61, 689 (1989)

Choice of the basis set

A periodic solid is a collection of atoms in periodically repeated positions

$R + \tau_s$
$\hookrightarrow$ position inside the unit cell
$\downarrow$
lattice vector $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\right] \varphi_{k,v}(r) = \varepsilon_{kv}\, \varphi_{kv}(r)$$

$V_{ext}(r)$, $n(r)$ ($\rightarrow V_H(r)$, $v_{xc}(r)$) are periodic functions

$$V_{ext}(r+R) = V_{ext}(r) \qquad n(r+R) = n(r)$$

$$V_{ext}(r) = \sum_{R,s} V_s\left(\vec{r} - (\vec{R} + \vec{\tau}_s)\right); \qquad V_s(\vec{r}) = -\frac{e^2 Z_s}{|\vec{r}|}$$

To solve the problem a basis set is introduced in order to expand the wavefunctions (in Bloch form)

$$\underset{kv}{\varphi}(r) = \sum_{i=1}^{N_b} c^i_{kv}\, b^k_i(\vec{r})$$

$\hookrightarrow$ basis function
$\hookrightarrow$ expansion coefficient

This brings the eigenvalues problem to matrix form

$$\left[H_{KS}^{(P,P)} - \varepsilon_{kv}\right] \varphi_{kv}(r) = 0$$

$$\downarrow$$

$$\sum_{j=1}^{Nb} \left[H^{(k)}_{ij} - \varepsilon_{kv} S^{(k)}_{ij}\right] c^j_{kv} = 0$$

$$H^{(k)}_{ij} = \langle b^{(k)}_i | H | b^{(k)}_j \rangle$$

$$S^{(k)}_{ij} = \langle b^{(k)}_i | b^{(k)}_j \rangle$$

A natural choice for a periodic system is given by the Plane Wave basis set

$$b_i^{(k)}(\vec{r}) = \langle r | k+G_i \rangle = \frac{1}{\sqrt{V}} e^{+i(k+G)r}$$

with $\vec{G}_i = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$ $\quad \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$

reciprocal lattice vectors

PW's form an infinite (and complete) orthogonal basis set. A finite basis set is selected requiring

$$\frac{\hbar^2}{2m}(k+G_i)^2 < E_{cutoff}$$

It has several advantages

- It is unbiased: has the same spatial resolution in every point and for every configuration
- can be improved easily and systematically by increasing Ecutoff
- Matrix elements are very simple to calculate

$$\langle k+G | -\frac{\hbar^2}{2m}\nabla^2 | k+G' \rangle = \frac{\hbar^2}{2m}(k+G)^2 \delta_{GG'}$$

$$\langle k+G | V(r) | k+G \rangle = \frac{1}{V}\int V(r)\, e^{-i(G-G')r} d^3r = \tilde{V}(G-G')$$

- Allows the use of FFT to go back and forth between direct and reciprocal space

$$\nabla^2 V_H(r) = -4\pi e^2 n(r)$$

$$n(r) \xrightarrow[N\ln N]{FFT} n(G) \xrightarrow[N]{} V_H(G) = \frac{4\pi e^2}{G^2} n(G) \xrightarrow[N\ln N]{FFT} V_H(r)$$

$$(H\varphi)(k+G): \quad T\varphi = \frac{\hbar^2}{2m}(k+G)^2 \varphi(k+G) \qquad N\varphi$$

$$\varphi(k+G) \xrightarrow[N\ln N]{FFT} \varphi(r) \xrightarrow[N]{} V(r)\varphi(r) \xrightarrow[N\ln N]{FFT} [V\varphi](k+G)$$

However a straightforward use of PW's is frustrated by the very large numbers needed to describe core electron wavefunctions

$$\langle r_{1s} \rangle \sim 1/Z \sim \lambda_{min}$$

$$G_{max} \sim \frac{2\pi}{\lambda_{min}} \sim 2\pi Z$$

$$E_{cutoff} \sim \frac{\hbar^2}{2m} G_{max}^2 \sim (2\pi Z)^2 \, Ryd$$

but core electrons do not pertecipate to chemical bonding and are almost unchanged with respect to the atomic case.

The region around the nuclei can and must be treated in a special way to make the size of the problem tractable. there are 2 strategies

① All-electrons methods: (F)LAPW, (F)LMTO, KKR

APW: The space is seperated in atomic spheres and the interstitial region. The basis set is given by plane waves in the interstitial region matched to atomic-like solutions on the spheres.

$$\mathscr{A}(\mathbf{p}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta, \varphi)\, R_l(E, r)\, \eta(r_s - r) + e^{i\mathbf{p}\cdot\mathbf{r}} \eta(r - r_s)$$

In this basis the secular equation becomes

$$\begin{aligned}\langle \mathscr{A}_{\mathbf{k}_i} | H - E | \mathscr{A}_{\mathbf{k}_j} \rangle &= \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \delta_{ij} \\ &+ \frac{4\pi r_s^2}{\Omega} \left\{ \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \frac{j_1(|\mathbf{k}_i - \mathbf{k}_j| r_s)}{|\mathbf{k}_i - \mathbf{k}_j|} \right. \\ &+ \left. \sum_{l=0}^{\infty} (2l+1)\, P_l(\cos\theta_{ij})\, j_l(k_i r_s)\, j_l(k_j r_s) \left[\frac{R_l'(E, r_s)}{R_l(E, r_s)} - \frac{j_l'(k_j r_s)}{j_l(k_j r_s)} \right] \right\}\end{aligned}$$

For practical purposes the logarithmic derivative

$\frac{R_\ell'(E,r_s)}{R_\ell(E,r_s)}$ is linearized around a reference energy. (Linearized Augmented Plane Waves)

and corrections due to the non-complete sphericity of the potential in the spheres can be added (Full-potential LAPW)

Similar strategies are used in (F)LMTO, KKR

In all these methods core electrons are solved inside the atomic spheres while valence electrons are solutions of the secular equation given by the matching of outer and inner solutions at the sphere boundary.

Pseudopotentials: Core states are eliminated and for valence electrons the inner solution is replaced with a smooth nodeless pseudo-wfc that has the same scattering properties (the same logarithmic derivatives). At this point there is no need to treat differently inner and outer regions an you can just expand in plane waves everywhere.

Hamman, Schlüter and Chiang Phys Rev Lett 43 1494 (1979) have shown that the good scattering properties can be obtained by norm-conserving pseudopotentials that also give the correct normalization of the (pseudo)-wfc

The price to be payed is the non-locality of the pseudopotentials (in the core region) i.e. wfc with different angular momenta see different pseudopotentials (in the core region)

This make computation of matrix elements more complex than for a local potentials but efficient schemes have been proposed

see for instance

L. Kleinman and D.H. Bylander, Phy. Rev. Lett 48 1425 (1982)

More on pseudopotentials

A. Qteish's lectures

More on All electrons methods

Bassani - Pastori Parravicini

"Electronic States and Optical transition in Solids"

Total Energy of an Infinite Periodic Solid

Let us write the expression for the total energy per cell of an infinite periodic Solid

$$\frac{E}{N_{cell}} = \frac{1}{N_{cell}} \left(T_e + E_H + E_{xc} + \int V(r)\, n(r)\, d^3r + V_{nn} \right)$$

The three electrostatic contributions individually diverge but give a finite result when taken together due to the charge neutrality of the system

$$\frac{1}{N_{cell}}\left(E_H + \int V(r)\, n(r)\, d^3r + V_{nn}\right) = \frac{1}{N_{cell}}\frac{1}{2}\int \frac{(\rho_{ion}(r) + \rho_{el}(r))\ (\rho_{ion}(r') + \rho_{el}(r'))}{|r - r'|}\, d^3r\, d^3r'$$

$$= \frac{\Omega}{2} \sum_G{}' \frac{4\pi}{G^2} \left|\rho_{ion}(G) + \rho_{el}(G)\right|^2$$

where $\sum' = \sum_{G\neq 0}$

Ω = volume of the unit cell

$$\rho(G) = \frac{1}{\Omega}\int \rho(r)\, e^{-iGr}\, d^3r$$

Each term gives a finite contribution if is computed including a uniform comensating background of charge density $\rho_b = \pm e \frac{N_{el}/cell}{\Omega}$ that kill the $G=0$ diverging component

Hartree Energy $\quad \frac{1}{N_{cell}} E_H = \frac{\Omega}{2} \sum_G{}' \frac{4\pi e^2}{G^2} |n(G)|^2$

Ext. pot Energy $\quad \frac{1}{N_{cell}} E_{ext} = \Omega \sum_G{}' V^*_{ext}(G)\, n(G)$

$$V_{ext}(G) = \frac{1}{\Omega}\int_\Omega \sum_{R,s} \frac{-Z_s e^2}{|r-(R+\tau_s)|} e^{-iGr} = -\frac{4\pi e^2}{G^2}\,\frac{\sum_s Z_s e^{-iG\tau_s}}{\Omega}$$

where $\{\tau_s\}$ are the atomic positions in the unit cell.

the infinite sums in the previous equations contain the $\frac{4\pi}{G^2}$ coulomb kernel that decays very slowly for large G. The convergence is granted by the vanishing of $n(G)$ (due to the smothnen of the density in real space). This is not the case for the ion-ion term that originates from pointlike charges.

in real space

$$\frac{1}{N_{cell}} V_{nn} = \frac{1}{N_{cell}} \frac{e^2}{2} \sum_{\substack{R R' \\ s s' \\ R+\tau_s \neq R'+\tau_{s'}}}' \frac{Z_s Z_{s'}}{|R+\tau_s - R' - \tau_{s'}|} = \frac{e^2}{2} \sum_{\substack{R \\ s, s' \\ R+\tau_s \neq \tau_{s'}}}' \frac{Z_s Z_{s'}}{|R+\tau_s - \tau_{s'}|}$$

in reciprocal space

$$\frac{1}{N_{cell}} V_{nn} = \frac{1}{2} \frac{4\pi e^2}{\Omega} \sum_G \frac{|\sum_s Z_s e^{-iG\tau_s}|^2}{G^2} \quad - \text{self interaction}$$

large r slow decay ⟷ small G divergence (no prob: neutral)

large G slow decay ⟷ small r divergence (no prob: no self-int)

In the Ewald method one exploit the good properties of each space by splitting the sum in two pieces

$$\frac{1}{r} = \frac{erf(\sqrt{\alpha} r)}{r} + \frac{1 - erf(\sqrt{\alpha} r)}{r} = \varphi_1(\sqrt{\alpha} r) + \varphi_2(\sqrt{\alpha} r)$$

$$\frac{4\pi}{G^2} = \frac{4\pi}{G^2} e^{-\frac{G^2}{4\alpha}} + \frac{4\pi}{G^2}\left(1 - e^{-\frac{G^2}{4\alpha}}\right)$$

φ_1 converge rapidly in G space, φ_2 converge rapidly in real space

$$\frac{1}{N_{cell}} V_{nn} = \frac{1}{2} \frac{4\pi e^2}{\Omega} \sum_G' \frac{e^{-\frac{G^2}{4\alpha}}}{G^2} \left| \sum_s Z_s e^{-iG\tau_s} \right|^2 - \frac{\pi e^2}{2\Omega\alpha} \left|\sum Z_s\right|^2 - e^2 \sum Z_s^2 \sqrt{\frac{\alpha}{\pi}}$$

$$+ \frac{e^2}{2} \sum_{\substack{R \\ s s'}}' Z_s Z_{s'} \varphi_2\left(\sqrt{\alpha} |R+\tau_s - \tau_{s'}|\right)$$

More on EWALD sums in

M. P. Tosi in Solid State Physics vol <u>16</u> p. 1.

In many instances sums (integrals) over the Brillouin Zone are needed.

In semiconductors and insulators occupied and empty bands are separated by an energy gap and sums over occupied states involves sums over the entire BZ

$$n(r) = \sum_{k,v,\sigma} |\varphi^\sigma_{kv}(r)|^2$$

$$T_S[n] = \sum_{k,v,\sigma} \langle \varphi^\sigma_{kv} | -\frac{\hbar^2}{2m}\nabla^2 | \varphi^\sigma_{kv} \rangle$$

These sums are performed using Special Points, i.e. discrete grids of k-points in the BZ that exploit the symmetry of the system to minimize the number of k-points where eigenvalues and eigenfunction must be calculated. Grids with quite few points are usually sufficient in insulators and semiconductors.

In metals, the presence of a Fermi surface makes the BZ sampling less rapidly converging.

Special points can still be used in combination with some density of state smearing technique.

A widely used alternative is the use of the linear tetrahedron method

Special Points
A. Baldereschi, Phy. Rev. B 7 5212 (1973)
D.J. Chadi and M.L. Cohen, Phys Rev B 8, 4547 (1973)
H.J. Monkhorst and J.D. Pack, Phys. Rev B 13, 5188 (1976)

Smearing
C-L. Fu and K-M. Ho Phys Rev B 28 5480 (1983)
M. Methfessel and A.T. Paxton, Phys Rev B 40 3613 (1989)

Tetrahedron method
J. Rath and A.J. Freeman Phys Rev B 11, 2109 (1975)

The energy expression can be written in another widely used form which makes use of the KS eigenvalue equations.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_0 + V_H + v_{xc}\right]\varphi_{k\nu}(r) = \varepsilon_{k\nu}\,\varphi_{k\nu}(r)$$

The sum over occupied states of the eigenvalues gives the "band structure" energy

$$E_{bs} = \frac{1}{N_k}\sum_{\substack{k\nu\\ \sigma}} \varepsilon^{\sigma}_{k\nu} = \frac{1}{N_k}\sum_{\substack{k\nu\\ \sigma}} \langle \varphi^{\sigma}_{k\nu} | -\frac{\hbar^2}{2m}\nabla^2 | \varphi^{\sigma}_{k\nu}\rangle + \int_{\Omega} [V_0 + V_H + v_{xc}]\, n(r)\, d^3r$$

That contains ① the kinetic energy ② the external potential energy ③ twice the Hartree energy ④ an average of the xc potential

The total energy can therefore be written as

$$E = \frac{1}{N_k}\sum_{\substack{k\nu\\ \sigma}} \varepsilon^{\sigma}_{k\nu} - E_H + \int_{\Omega} [\epsilon_{xc} - v_{xc}]\, n(r)\, d^3r + E_{Ewald}$$

Reaching the Self-Consistent solution.

Kohn-Sham equations are self consistent eqs.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right]\varphi_i(r) = \varepsilon_i\,\varphi_i(r)$$

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

$$V_{KS}(r) = V_0(r) + e^2\int\frac{n(r')}{|r-r'|}\,d^3r' + v_{xc}^{LDA}(n(r))$$

Given a trial potential $V_{KS}^{(in)}(r)$ they produce an output density and an output potential $V_{KS}^{(out)}(r)$.
The self-consistent solution that minimizes the energy is obtained when $V_{KS}^{(out)}(r) = V_{KS}^{(in)}(r)$.

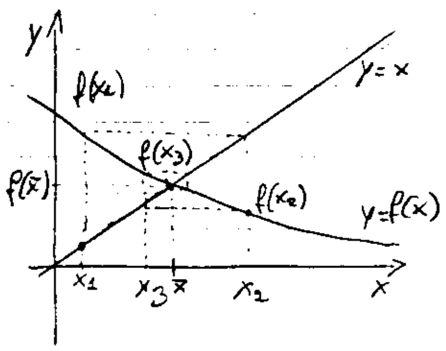
It is a problem in which the fixed point is searched

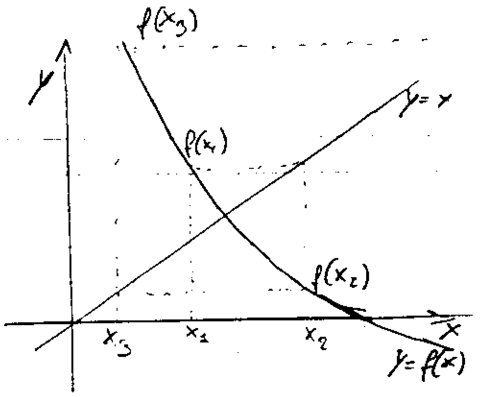
$x = f(x)$

an obvious strategy to find the fixed point is to start from some guess x_0 and then iterate the equation

$x_{m+1} = f(x_m)$

if the procedure converges the limit value is the searched fixed point $\bar{x} = f(\bar{x})$. The success of the procedure depends on the shape of the function $f(x)$





If the slope of $f(x)$ is too large and negative the simple iteration procedure does not convenverge.

The procedure does not converge either if the slope is positive but this is not our case since

$$\frac{\delta V^{out}(r)}{\delta V^{in}(r')} = e^2 \int \frac{1}{|r-r''|} \frac{\delta n(r'')}{\delta V^{in}(r')} + \frac{d v_{xc}(n(r))}{dn} \frac{\delta n(r)}{\delta V^{in}(r')}$$

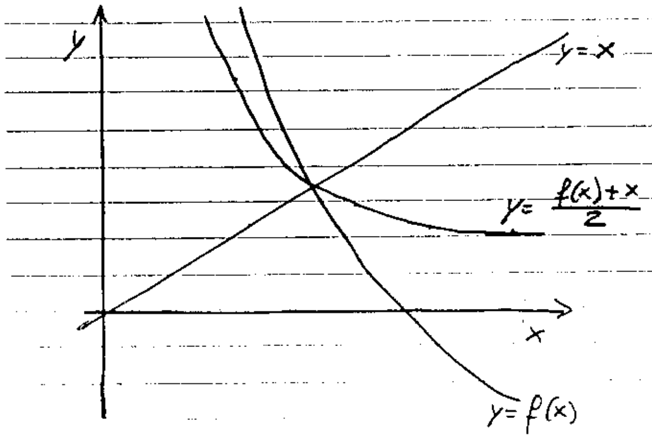
is negative definite

as $\frac{\delta n(r)}{\delta V(r')} = \chi_0(r,r')$ is negative definite too (if you increase the potential, electrons flow away).

The slope may be very large due to the $\frac{1}{G^2}$ divergence of the coulomb term.

It is always a good idea to damp the iterations with a friction coefficient α that improve convergence.

$$x_{m+1} = \alpha f(x_m) + (1-\alpha) x_m$$



$$V^{(in)}_{m+1}(r) = \alpha V^{(out)}_m(r) + (1-\alpha) V^{(in)}_m(r)$$ simple mixing

In general more complex mixing scheme (Anderson or Broyden mixing) are used that involve a number (3-4) of previous iteration to guess the local shape of $f(x)$

More on Mixing

D.G. Anderson, J. Assoc. Comput. Mach. 12 547 (1964)

D. D. Johnson, Phys. Rev. B 38 12807 (1988)

Other minimization strategies

The solution of a set of Self Consistent equations is nothing but a procedure to minimize the total energy functional. Other schemes directly minimize it with respect to variation of the wavefunctions (with the orthogonality constraint), applying some general minimization strategies.

The simplest among them, not very efficient, is the steepest descent method in which the minimum is reached by a series of downhill steps in the direction of the local gradient.

$$E = \sum_i \langle \varphi_i | -\frac{\hbar^2}{2m} | \varphi_i \rangle + E_H[n] + E_{xc}[n] + \int V_0(r)\, n(r)\, d^3r + V_{nn}$$

$$- \sum_{ij} \lambda_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right)$$

$$\varphi_i'(r) = -\frac{\partial E}{\partial \varphi_i^*} = -\left\{ \left[-\frac{\hbar^2}{2m}\nabla^2 + V_0 + V_H + V_{xc} \right] \varphi_i - \sum_j \lambda_{ij} \varphi_j \right\}$$

$$\varphi_i^{(m+1)}(r) = \varphi_i^{(m)}(r) + \Delta\, \varphi_i'(r) \qquad + \text{ orthogonalization}$$

It may take hundreds of steps to reach the minimum. More sofisticated schemes are variants of conjugate gradient minimizations.

More on global minimizations:

R. Car and M. Parrinello Phys. Rev. Lett <u>55</u> 2471 (1985)

M.C. Payne, M.P. Teter, D.C. Allen, T.A. Arias and J.D. Joannopoulos Rev. Mod. Phys. <u>64</u> 1045 (1992)

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3-6 The augmented plane wave method

3-6a *Description of the method*

The augmented plane wave method (APW method) was originally suggested by Slater[25] in 1937 to overcome the difficulty of satisfying boundary conditions inherent to the cellular method.

To describe the method we consider, for simplicity, the case of crystals containing one atom per unit cell. In the APW method the crystal potential is assumed to be spherically symmetric inside spheres surrounding the atoms (or ions) of radius r_s and constant outside (muffin-tin potential). For convenience we may take the value of the potential outside the spheres to be zero by an appropriate choice of the zero of the energy scale.

An eigenfunction $\psi(\mathbf{k}, \mathbf{r})$ with energy $E(\mathbf{k})$ can be expanded within the Wigner–Seitz cell in the form

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm}(\mathbf{k})\, Y_{lm}(\theta, \varphi)\, R_l(E, r)\, \eta(r_s - r) + \sum_j b_j(\mathbf{k})\, e^{i(\mathbf{k}+\mathbf{b}_j)\cdot\mathbf{r}}\, \eta(r - r_s), \tag{3-43}$$

where r, θ, φ are the polar coordinates of $\mathbf{r}$ with respect to the centre of the cell, and the function

$$\eta(x) = \begin{cases} 0 & \text{for } x \text{ negative,} \\ 1 & \text{for } x \text{ positive,} \end{cases}$$

is used. As in the cellular method, $R_l(E, r)$ is the solution of the radial wave equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR_l}{dr}\right) + \left[\frac{2m}{\hbar^2}(E - V(r)) - \frac{l(l+1)}{r^2}\right] R_l = 0,$$

which is regular at the origin. $V(r)$ denotes the muffin-tin potential within the sphere of radius r_s. The function $R_l(E, r)$ can be explicitly determined by numerical integration of the differential equation from the origin outwards for a range of E and l values.

In (3-43) the eigenfunction $\psi(\mathbf{k}, \mathbf{r})$ is seen to be expanded in spherical waves within the region where the potential is atomic-like, and in plane waves in the region where the potential is constant. The boundary conditions (3-42) at the surface of the Wigner–Seitz cell are automatically satisfied, and a much easier matching problem at the sphere surface provides the eigenvalues more efficiently than in the cellular method.

To see how to match solutions inside the sphere with those outside, let us consider the function

$$\mathscr{A}(\mathbf{p}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta, \varphi)\, R_l(E, r)\, \eta(r_s - r) + e^{i\mathbf{p}\cdot\mathbf{r}}\, \eta(r - r_s) \tag{3-44a}$$

and choose the coefficients a_{lm} in such a way that $\mathscr{A}(\mathbf{p}, \mathbf{r})$ is continuous. By expanding the plane wave $e^{i\mathbf{p}\cdot\mathbf{r}}$ in spherical harmonics (see Section 3-3b) and requiring the continuity of $\mathscr{A}(\mathbf{p}, \mathbf{r})$ at $r = r_s$,

$$a_{lm} = 4\pi Y^*_{lm}(\theta_{\mathbf{p}}, \varphi_{\mathbf{p}}) \frac{j_l(pr_s)}{R_l(E, r_s)}. \tag{3-44b}$$

The function (3-44a) with the choice of coefficients as given in (3-44b) is called and augmented plane wave. An augmented plane wave is a continuous function but, in general, a discontinuity in the slope at $r = r_s$ remains.

Expansion (3-43) can now be written in the equivalent form

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_j a_j(\mathbf{k})\, \mathscr{A}(\mathbf{k} + \mathbf{h}_j, \mathbf{r}), \tag{3-45}$$

where $\mathscr{A}(\mathbf{k} + \mathbf{h}_j, \mathbf{r})$ indicates the augmented plane wave of vector $\mathbf{k} + \mathbf{h}_j$. Though the expansion functions $\mathscr{A}(\mathbf{k} + \mathbf{h}_j, \mathbf{r})$ are discontinuous in slope at $r = r_s$, the function $\psi(\mathbf{k}, \mathbf{r})$ must be well behaved. By substituting the above expansion in the Schrödinger equation and using the variational procedure with respect to coefficients a_j of (3-45), the following matrix equation is obtained:

$$\| \langle \mathscr{A}_{\mathbf{k}_i} | H - E | \mathscr{A}_{\mathbf{k}_j} \rangle \| = 0, \tag{3-46}$$

where $\mathscr{A}_{\mathbf{k}_i}$ is a shorthand notation for $\mathscr{A}(\mathbf{k} + \mathbf{h}_i, \mathbf{r})$.

The explicit evaluation of matrix elements in (3-46) requires some care because of the discontinuity in slope of the trial wave functions at $r = r_s$. For precise details of their evaluation we refer the reader to Loucks;[26] the matrix elements in this account are derived from rigorous variational principles developed by Schlosser and Marcus[27] for discontinuous trial functions. A more direct derivation is given in the original work of Slater,[25] whose results we record here for the case of one atom per unit cell:

$$\begin{aligned} \langle \mathscr{A}_{\mathbf{k}_i} | H - E | \mathscr{A}_{\mathbf{k}_j} \rangle &= \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \delta_{ij} \\ &+ \frac{4\pi r_s^2}{\Omega} \left\{ \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \frac{j_1(|\mathbf{k}_i - \mathbf{k}_j| r_s)}{|\mathbf{k}_i - \mathbf{k}_j|} \right. \\ &\left. + \sum_{l=0}^{\infty} (2l + 1)\, P_l(\cos\theta_{ij})\, j_l(k_i r_s)\, j_l(k_j r_s) \left[\frac{R_l'(E, r_s)}{R_l(E, r_s)} - \frac{j_l'(k_j r_s)}{j_l(k_j r_s)} \right] \right\} \end{aligned} \tag{3-47}$$

where Ω indicates the volume of the unit cell, θ_{ij} indicates the angle between the wave vectors $\mathbf{k}_i$ and $\mathbf{k}_j$, j_l are the spherical Bessel functions, and P_l the Legendre polynomials. The matrix elements contain energy E both explicitly and implicitly through the logarithmic derivatives R_l'/R_l of the radial wave functions $R_l(E, r)$ at the sphere surface. The muffin-tin potential $V(r)$ enters expression (3-47) implicitly because it determines, for a given E, the quantity R_l'/R_l.

For practical calculations, one limits the expansion (3-45) to augmented plane waves with momenta smaller than a fixed value. The determinant (3-46) is then plotted as a function of E and eigenvalues are obtained as the zeros of the curve. The convergence of the procedure can be tested by adding more augmented plane waves in (3-45); the convergence is in general rapid, a number of 10–20 augmented plane waves being sufficient in most practical cases. As usual, group theory can be applied to obtain symmetry adapted combinations of augmented plane waves at $\mathbf{k}$ vectors of high symmetry.

3-6b *Discussion of the APW method*

The APW method has become in recent years one of the most powerful tools for studying electronic states in crystals. Although it was developed in 1937, it is only recently that the availability of large computers has allowed extensive studies with this method. In comparison with the tight binding or OPW methods, which require only relatively simple techniques (diagonalization of determinants of the form $\|A_{ij} - EB_{ij}\| = 0$

with A_{ij} and B_{ij} independent of E), the APW method presents an additional difficulty in that the matrix elements are complicated functions of the energy, as can be seen from the expression (3-47). On the other hand, the OPW determinants are usually much larger in size than those of the APW method.

In the APW method the crystal potential has to be approximated by a muffin-tin type potential. Though in most crystals this approximation is expected to be reasonable, it is, at least in principle, the least satisfactory aspect of the method.[28] In some cases, because of the difficulties associated with the tail of the atomic-like potential, it is convenient to consider the average potential outside the spheres as a disposable parameter to fit experimental results, similar to the situation previously described concerning $V(0)$ in the OPW method.

One good feature of the APW method with respect to the OPW (or tight binding method) is that no assumption about the core states is necessary. In cases such as transition metals, where the separation of the crystal states in well-localized core states from the spread-out valence states is questionable, the APW method can instead be applied successfully.

3-7 Green's function method

Green's function method was proposed originally by Korringa (1947), Kohn and Rostoker (1954), and Morse (1956), in different though equivalent forms.[29] Basically the method uses Green's function technique to transform the Schrödinger equation into an equivalent integral equation. This method avoids the difficulties concerning the problem of boundary conditions as in the cellular method, but the approximation of the crystal potential by a muffin-tin model potential is required.

For simplicity, we illustrate Green's function method in the case of crystals with one atom per unit cell. In order to calculate the crystal states of wave vector $\mathbf{k}$ in the first Brillouin zone, we determine Green's function $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E)$ which satisfies the equation

$$\left(\frac{\hbar^2}{2m}\nabla^2 + E\right) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E) = \delta(\mathbf{r} - \mathbf{r}') \tag{3-48}$$

and the boundary conditions:

$$G_{\mathbf{k}}(\mathbf{r} + \boldsymbol{\tau}_n, E) = e^{i\mathbf{k} \cdot \boldsymbol{\tau}_n} G_{\mathbf{k}}(\mathbf{r}, E) \tag{3-49}$$

required by the Bloch theorem. Using standard techniques[30] for a Green's function calculation, we expand $G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E)$ in terms of the set of eigenfunctions of the operator $(\hbar^2/2m)\nabla^2 + E$, satisfying the appropriate boundary conditions. We can now write

$$G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E) = \sum_{n} a_n(\mathbf{k}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{h}_n) \cdot (\mathbf{r}-\mathbf{r}')}, \tag{3-50}$$

where Ω is the volume of the unit cell. The coefficients of the expansion (3-50) are easily determined by direct substitution into (3-48):

$$G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E) = -\frac{1}{\Omega}\sum_{n} \frac{e^{i(\mathbf{k}+\mathbf{h}_n) \cdot (\mathbf{r}-\mathbf{r}')}}{\dfrac{\hbar^2}{2m}(\mathbf{k} + \mathbf{h}_n)^2 - E}. \tag{3-51}$$

The Schrödinger equation

$$\left(\frac{\hbar^2}{2m}\nabla^2 + E\right)\psi(\mathbf{k}, \mathbf{r}) = V(\mathbf{r})\,\psi(\mathbf{k}, \mathbf{r})$$

for crystal states of vector **k** is transformed, as in scattering theory, into the integral equation

$$\psi(\mathbf{k}, \mathbf{r}) = \int_{\Omega} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E)\, V(\mathbf{r}')\,\psi(\mathbf{k}, \mathbf{r}')\, d\mathbf{r}'. \tag{3-52}$$

To proceed further we explicitly assume a muffin-tin form for the crystal potential and set this potential equal to zero outside the sphere. Equation (3-52) can now be written in the form

$$\psi(\mathbf{k}, \mathbf{r}) = \int_{\Omega_s} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}', E)\, V(r')\,\psi(\mathbf{k}, \mathbf{r}')\, d\mathbf{r}', \tag{3-53}$$

where Ω_s indicates the volume of the inscribed sphere and $V(r')$ is the muffin-tin potential. We can expand $\psi(\mathbf{k}, \mathbf{r})$ inside the sphere in the form (3-40). Substituting (3-40) into the integral equation (3-53), we obtain a determinant compatibility relation whose solutions give the eigenvalues E and the coefficients c_{lm} of the eigenfunction expansions. The derivation of the compatibility relations is somewhat laborious, and we record here (for the case of one atom per unit cell) only the results as obtained by Slater using Ziman's procedure.[31] The matrix elements of Green's function method can be written as

$$M_{ij} = \left(\frac{\hbar^2}{2m}\mathbf{k}_i\cdot\mathbf{k}_j - E\right)\delta_{ij} + \frac{4\pi r_s^2}{\Omega}\left\{\sum_l (2l + 1)\, P_l(\cos\theta_{ij})\, j_l(k_i r_s)\, j_l(k_j r_s)\right.$$

$$\left.\times\left[\frac{R_l'(E, r_s)}{R_l(E, r_s)} - \frac{j_l'(kr_s)}{j_l(kr_s)}\right]\right\}, \tag{3-54}$$

where $\mathbf{k}_i = \mathbf{k} + \mathbf{h}_i$ and $(\hbar^2/2m)\,k^2 = E$, E being the eigenvalue of the secular equation. The meaning of other symbols adopted in (3-54) is the same as in (3-47) for the APW method. This form is particularly suitable for bringing out the connection with other methods. In Green's function, as in the APW method, the muffin-tin potential enters implicitly into the expression for the matrix elements through the logarithmic derivative R_l'/R_l of the radial wave functions $R_l(E, r)$ at the sphere radius. The term $((\hbar^2/2m)\,\mathbf{k}_i\cdot\mathbf{k}_j - E)\,\delta_{ij}$ and the term with R_l'/R_l are identical in both expressions (3-54) and (3-47); the extra term $j_1(|\mathbf{k}_i - \mathbf{k}_j|\, r_s)/|\mathbf{k}_i - \mathbf{k}_j|$ appears in (3-47), however, and the argument of j_l'/j_l is at k in (3-54) whereas it is at k_j in (3-47).

The basic principles of Green's function method are very similar to those of the APW method. Both methods can be used to solve the problem of the motion of electrons in a muffin-tin model potential. It has been established by Segall and Burdick[32] that the two methods lead to equal results when the same muffin-tin potential is considered. Furthermore a common theoretical framework for these two methods has been established by Ziman on the basis of a pseudopotential formalism,[31] similar to that described for the OPW method. In this formalism the muffin-tin potential is replaced by an "effective" potential which is zero everywhere except at the sphere surfaces, where it exhibits an energy and l-dependent singularity.