Single-particle basis sets for realistic theories of correlated materials:

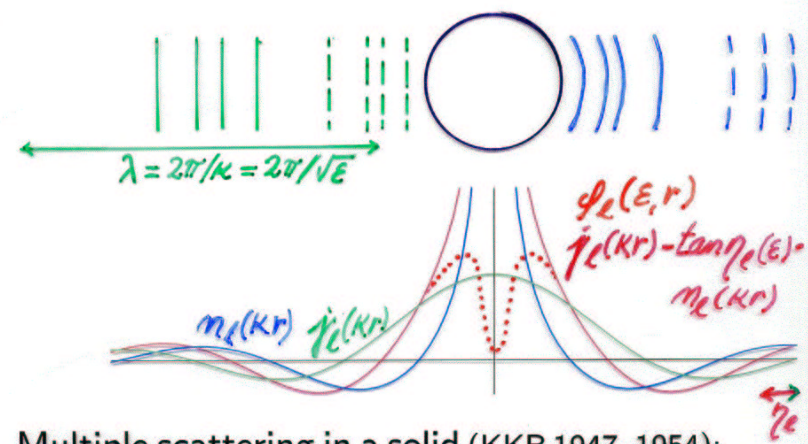
Current construction:
The single-particle Hilbert space is derived from a (Kohn-Sham) potential and a subspace of *localized* orbitals is separated for the *correlated* electrons

Third-Generation MTOs

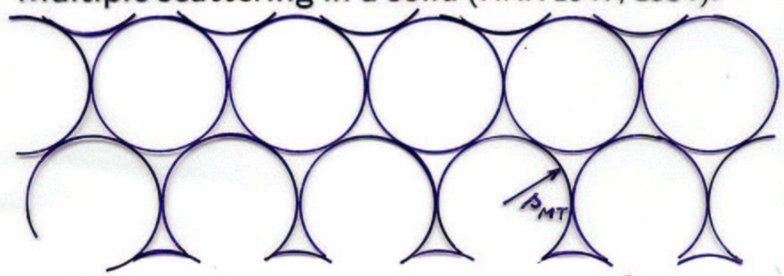
D. Savrasov, S. Ezhov, T. Saha-Dasgupta, C. Arcangeli, R.W. Tank, G. Krier, O. Jepsen, O.K. Andersen.

Max-Planck-Institut FKF, Stuttgart, FRG.
http://www.mpi-stuttgart.mpg.de
PR B 62, 16219 (2000)

Elastic scattering from a single atom:



Multiple scattering in a solid (KKR 1947, 1954):



$$\sum_{Rlm}\left[S_{R'l'm',Rlm}(\varepsilon)-\delta_{R'l'm',Rlm}\kappa\cot\eta_{Rl}(\varepsilon)\right]v_{Rlm}=0$$

$$\sum_{lm}\left[S_{l'm',lm}(\mathbf{k},\varepsilon)-\delta_{l'm',lm}\kappa\cot\eta_{l}(\varepsilon)\right]v_{lm}=0$$

$$MTO \propto \begin{cases} n - ij, & r \geq s_{MT} \\ (j-\varphi)_\kappa \cot\eta - ij, & r \leq s_{MT} \end{cases}$$

Multiple-scattering theory for spherical potential scatterers:
As irregular solution of the radial wave-equation, choose the *Hankel fct:*

$$h_l(\varepsilon,r) \equiv -i\kappa^{l+1}h_l^{(1)}(\kappa r) = \kappa^{l+1}\left[n_l(\kappa r) - i j_l(\kappa r)\right]$$
$$\equiv n_l(\varepsilon,r) - i\kappa j_l(\varepsilon,r), \qquad \kappa \equiv \varepsilon^{\frac{1}{2}},$$

which *decays* exponentially as a function of r for $0 < \arg\varepsilon < 2\pi$,
is analytical for $0 \leq \arg\varepsilon < 2\pi$, and is real for negative ε.
$j_l(\varepsilon,r)$ (regular) and $n_l(\varepsilon,r)$ (irregular) are real for real ε.
The *bare* MTO for a scatterer with *phase shifts* $\eta_l(\varepsilon)$ and regular solutions $\varphi_l(\varepsilon,r)$ of the radial Schrödinger equations, is:

$$\phi_{lm}(\varepsilon,\mathbf{r}) \equiv Y_{lm}(\hat{\mathbf{r}})\begin{cases} h_l(\varepsilon,r) = n_l(\varepsilon,r) - i\kappa j_l(\varepsilon,r) & r \geq s \\ \varphi_l(\varepsilon,r) + \kappa\cot\eta_l(\varepsilon)\, j_l(\varepsilon,r) - i\kappa j_l(\varepsilon,r) & r \leq s \end{cases}$$
$$= Y_{lm}(\hat{\mathbf{r}})\left[\varphi_l(\varepsilon,r) - \varphi_l^o(\varepsilon,r)\right] + Y_{lm}(\hat{\mathbf{r}})\, h_l(\varepsilon,r)$$

$\varphi_l(\varepsilon,r)$ and $\kappa\cot\eta_l(\varepsilon)$ are real for real ε. $\varphi_l^o(\varepsilon,r) \equiv n_l(\varepsilon,r) - \kappa\cot\eta_l(\varepsilon)\, j_l(\varepsilon,r)$
$\varphi_l(\varepsilon,r) - \varphi_l^o(\varepsilon,r)$ vanishes smoothly for $r \to s$.

For a solid with sites R, condition for solution of Scrödinger's eqn at ε :

$$\mathcal{P}_{R'l'm'}(r)\sum_{Rlm}^{\neq R'} c_{Rlm}\, h_{Rlm}(\varepsilon,\mathbf{r}-\mathbf{R}) = c_{R'l'm'}\left[-\kappa\cot\eta_{R'l'}(\varepsilon) + i\kappa\right] j_{l'}(\varepsilon,r)$$

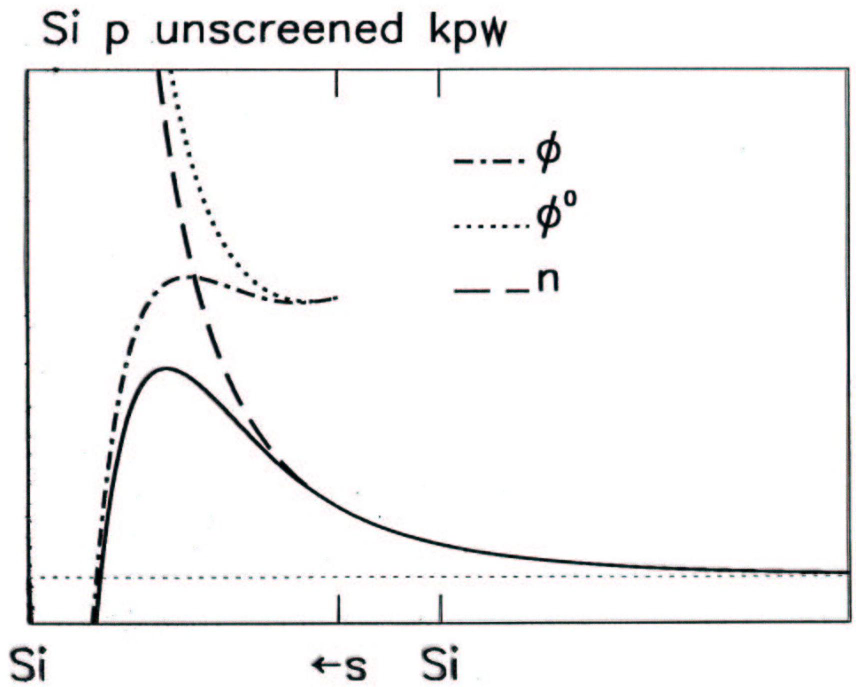
for all $R'l'm' \equiv R'L'$. This expresses tail-cancellation. Project onto $\mathbf{R}' \neq \mathbf{R}$:

$$\mathcal{P}_{R'L'}(r)\; h_l(\varepsilon,|\mathbf{r}-\mathbf{R}|)\, Y_L\left(\widehat{\mathbf{r}-\mathbf{R}}\right) \equiv \mathcal{P}_{R'L'}(r)\; h_L(\varepsilon,\mathbf{r}-\mathbf{R}) =$$
$$j_{l'}(\varepsilon,r)\sum\nolimits_{l''} 4\pi C_{LL'l''}\, i^{-l+l'-l''}\kappa^{l-l'-l''}\, h_{l''\,m'-m}\left(\varepsilon,\mathbf{R}-\mathbf{R}'\right) \equiv$$
$$j_{l'}(\varepsilon,r)\, S_{R'L',RL}(\varepsilon) = j_{l'}(\varepsilon,\mathbf{r})\left[S_{n;R'L',RL}(\varepsilon) - i\kappa S_{j;R'L',RL}(\varepsilon)\right]$$

$S(\varepsilon)$ is the *bare structure matrix*. On-site elements $\equiv -i\kappa\delta_{LL'}$.
For ε real, $S_n(\varepsilon)$ and $S_j(\varepsilon)$ are real and symmetric. The tail-cancellation condition gives rise to the linear, homogeneous KKR equations:

$$0 = \sum_{RL}\left[S_{R'L',RL}(\varepsilon_i) + \kappa\cot\eta_{Rl}(\varepsilon_i)\,\delta_{R'R}\delta_{L'L}\right] c_{RL,i} \equiv \sum_{RL} K_{R'L',RL}(\varepsilon_i)\, c_{RL,i}$$

for all $R'L'$. Good l-convergence because $\eta_l(\varepsilon) = 0$ for $l \gtrsim 3$.



The set of *screened* spherical waves are solutions of the wave-equation:

$$h^{\alpha}_{RL}\left(\varepsilon,\mathbf{r}-\mathbf{R}\right)=\sum_{\bar{R}\bar{L}}h_{\bar{R}\bar{L}}\left(\varepsilon,\mathbf{r}-\bar{\mathbf{R}}\right)\,M^{\alpha}_{\bar{R}\bar{L},RL}\left(\varepsilon\right),$$

with specified phase shifts, $\alpha_{RL}\left(\varepsilon\right)$ –*the medium*– in all *other* channels:

$$j^{\alpha}_{RL}\left(\varepsilon,r\right)\equiv j_{l}\left(\varepsilon,r\right)-\frac{\tan\alpha_{RL}\left(\varepsilon\right)}{\kappa}n_{l}\left(\varepsilon,r\right)$$

$$\mathcal{P}_{R'L'}\left(r\right)h^{\alpha}_{RL}\left(\varepsilon,\mathbf{r}-\mathbf{R}\right)=n_{l}\left(\varepsilon,r\right)\delta_{R'R}\delta_{L'L}+j^{\alpha}_{R'L'}\left(\varepsilon,r\right)S^{\alpha}_{R'L',RL}\left(\varepsilon\right)$$

$$=\;n_{l'}\left(\varepsilon,r\right)\left[\delta_{R'R}\delta_{L'L}-\frac{\tan\alpha_{R'L'}\left(\varepsilon\right)}{\kappa}S^{\alpha}_{R'L',RL}\left(\varepsilon\right)\right]+j_{l'}\left(\varepsilon,r\right)S^{\alpha}_{R'L',RL}\left(\varepsilon\right)$$

$$\mathcal{P}_{R'L'}\left(r\right)h^{\alpha}_{RL}\left(\varepsilon,\mathbf{r}-\mathbf{R}\right)=\sum_{\bar{R}\bar{L}}\left[n_{l'}\left(\varepsilon,r\right)\delta_{R'\bar{R}}\delta_{L'\bar{L}}+j_{l'}\left(\varepsilon,r\right)S_{R'L',\bar{R}\bar{L}}\left(\varepsilon\right)\right]M^{\alpha}_{\bar{R}\bar{L},RL}$$

$$M^{\alpha}\left(\varepsilon\right)=1-\frac{\tan\alpha\left(\varepsilon\right)}{\kappa}S^{\alpha}\left(\varepsilon\right),\qquad S^{\alpha}\left(\varepsilon\right)^{-1}=S\left(\varepsilon\right)^{-1}+\frac{\tan\alpha\left(\varepsilon\right)}{\kappa}$$

$$S^{\alpha}(\varepsilon) = \kappa \cot\alpha(\varepsilon) - \kappa \cot\alpha(\varepsilon)\left[S(\varepsilon) + \kappa\cot\alpha(\varepsilon)\right]^{-1} \kappa\cot\alpha(\varepsilon)$$

Re $h^{\alpha}(\varepsilon, \mathbf{r})$ is a solution for the *inhomogeneous* boundary condition:

: $n(\kappa, r)$ in the *eigen*-channel and $\propto j^{\alpha}(\kappa, r)$ in all *other* channels.

Im $h^{\alpha}(\varepsilon, \mathbf{r})$ is a solution for the *homogeneous* boundary condition:

: $\propto j^{\alpha}(\kappa, r)$ in *all* channels.

Im $h^{\alpha}(\varepsilon, \mathbf{r}) = 0$ and Im $S^{\alpha}(\varepsilon) = 0$ for all energies where the medium has no eigenvalues. Those are the energies, for which $h^{\alpha}(\varepsilon, \mathbf{r})$ is *localized* and weakly energy dependent and for which we can generate the *screened structure matrix*, $S^{\alpha}(\varepsilon)$, in real space.

The *screened* KKR equations become:

$$0 = \sum_{RL}\left[S^{\alpha}_{R'L',RL}(\varepsilon_i) + \kappa\cot\eta^{\alpha}_{Rl}(\varepsilon_i)\,\delta_{R'R}\delta_{L'L}\right] c^{\alpha}_{RL,i} \equiv \sum_{RL} K^{\alpha}_{R'L',RL}(\varepsilon_i)\, c^{\alpha}_{RL,i}$$

where the phase shifts with respect to the medium are given by:

: $\tan\eta^{\alpha}_{l}(\varepsilon) = \tan\eta_{l}(\varepsilon) - \tan\alpha_{RL}(\varepsilon)$.

Screened MTOs = kinked partial waves (KPWs) = NMTOs with N=0:

$$\phi^{\alpha}_{RL}(\varepsilon, \mathbf{r}-\mathbf{R}) =$$
$$\left[\varphi^{\alpha}_{RL}(\varepsilon, |\mathbf{r}-\mathbf{R}|) - \varphi^{o\alpha}_{RL}(\varepsilon, |\mathbf{r}-\mathbf{R}|)\right] Y_L\left(\widehat{\mathbf{r}-\mathbf{R}}\right) + h^{\alpha}_{RL}(\varepsilon, \mathbf{r}-\mathbf{R})$$

Partition the RL-channels into *active* (A) and *passive* (P) channels:

RL	$\alpha(\varepsilon)$	subst the irregular $j^{\alpha}_{RL}(\varepsilon, r)$ by	
$A:$	$0 \equiv j^{\alpha}_{RL}(\varepsilon, a_R)$	0	kink
$P:$	$\alpha_{RL}(\varepsilon) \equiv \eta_{Rl}(\varepsilon)$	$c_1 \cdot \varphi_{Rl}(\varepsilon, r)$	smooth

A-channels are chosen to give localization by means of *confining* –or *hard*– spheres of radii, a_R. Upon a renormalization, $K^{\alpha} \rightarrow$ kink matrix.

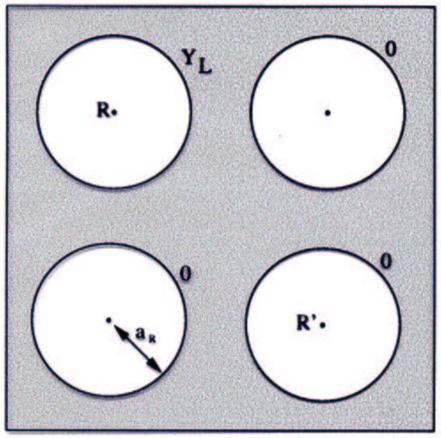
P-channels only contribute to MTO tails and are deleted from the screened KKR equations, which say that the superposition of active kinked partial waves should be smooth, because $\kappa\cot\eta^{\alpha}_{P} = \infty$.

Screened spherical waves: SSW's

Position a spherical wave (i.e a multipole)

$$Y_L(\theta,\phi)n_l(\kappa r)$$

at site $\mathbf{R}$. Screen at all other sites $\mathbf{R}'$



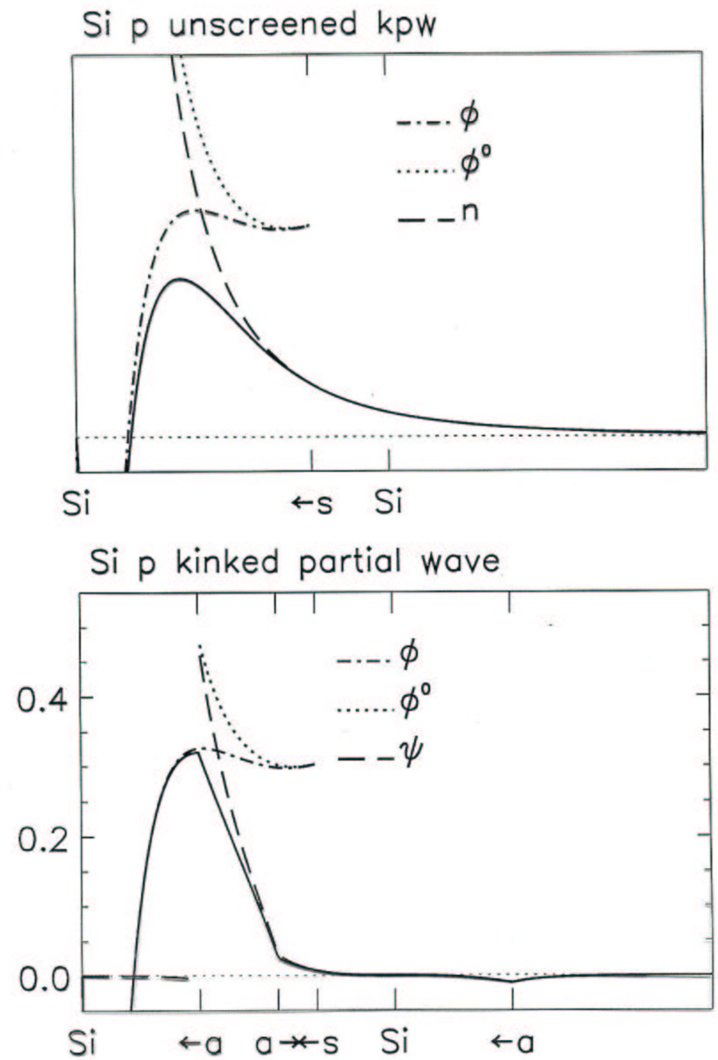
$a_{\mathbf{R}}$ = hard core radii (non-overlapping)

Mathematical definition:

$$\nabla^2|\psi\rangle \quad = \quad -\kappa^2|\psi\rangle$$

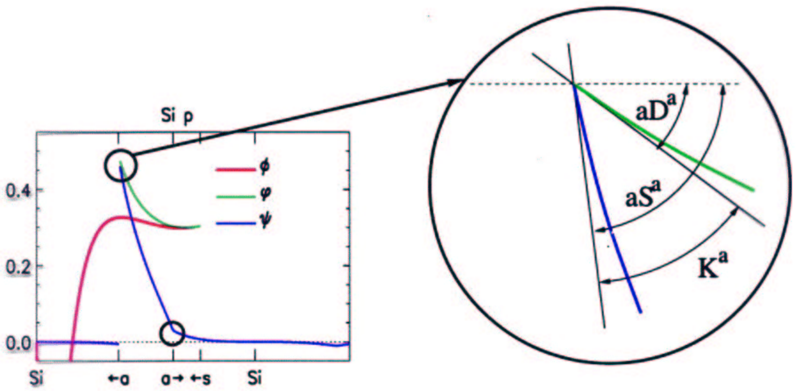
boundary conditions:

$$|\psi_{\mathbf{R}L}(a_{\mathbf{R}'})\rangle \quad = \quad \delta_{\mathbf{R},\mathbf{R}'}\,\delta_{L,L'}\,Y_L$$



Kink Matrix

$$K^{a}_{Rlm,R'l'm'}(\varepsilon)$$

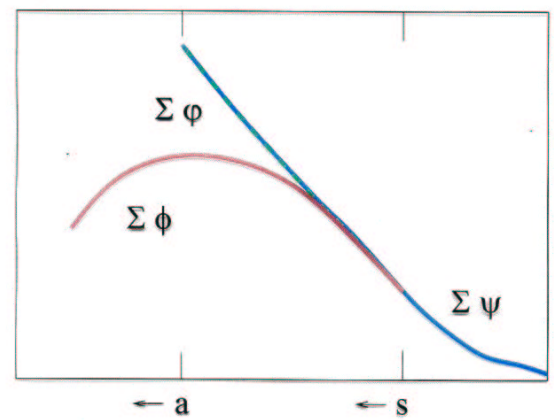


Make superposition of kinked partial waves.

Demand kink cancellation ⇒

Screened KKR equations

$$\sum_{RL} K_{R'L',RL}(\varepsilon)\, c_{RL} = 0$$



Since $K^a(\varepsilon)$ gives the kinks of the set of kinked partial waves $\phi^a(\varepsilon,\mathbf{r})$,

$$(\mathcal{H}-\varepsilon)\,\phi^a_{R'L'}(\varepsilon,\mathbf{r}) = -\sum_{RL\in A}\delta(r_R-a_R)\,Y_L(\hat{\mathbf{r}}_R)\,K^a_{RL,R'L'}(\varepsilon)$$

Defining a Green matrix: $G^a(\varepsilon)\equiv K^a(\varepsilon)^{-1}$, we get:

$$(\mathcal{H}-\varepsilon)\sum_{R'L'\in A}\phi^a_{R'L'}(\varepsilon,\mathbf{r})\,G^a_{R'L',RL}(\varepsilon) = -\delta(r_R-a_R)\,Y_L(\hat{\mathbf{r}}_R)$$

which is a contraction onto the hard spheres of the definition,

$$(\mathcal{H}_{\mathbf{r}}-\varepsilon)\,G\left(\varepsilon,\mathbf{r},\mathbf{r}'\right) = -\delta\left(\mathbf{r}-\mathbf{r}'\right)$$

of the Green function. The contracted Green function,

$$\gamma^a_{RL}(\varepsilon,\mathbf{r})\equiv\sum_{R'L'\in A}\phi^a_{R'L'}(\varepsilon,\mathbf{r})\,G^a_{R'L',RL}(\varepsilon)$$

has kink 1 in the own (RL) channel, is smooth everywhere else, and has poles at the eigenvalues.

Down and up-folding:

In order that the MTOs transform linearly among each other upon the downfolding, we keep the radii a_R constant, and almost touching (ionic). In the following, b refers to a "complete" representation with active channels B including all atoms and $l\lesssim 3$. a refers to a down-folded representation with active channels A, a subset of B: $\quad B=A+I.$

From their definition, the two *contracted* Green functions, $\gamma^a_{RL}(\varepsilon,\mathbf{r})$ and $\gamma^b_{RL}(\varepsilon,\mathbf{r})$, are *identical* for $RL\in A$, but the functions with $RL\in I$ exist only in the b-set and not in the a-set.

$$\phi^a(\varepsilon,\mathbf{r})\,G^a(\varepsilon)=\gamma_A(\varepsilon,\mathbf{r})=\phi^b_A(\varepsilon,\mathbf{r})\,G^b_{AA}(\varepsilon)+\phi^b_I(\varepsilon,\mathbf{r})\,G^b_{IA}(\varepsilon)$$

Partitioning yields for respectively b and a:

$$\left\{\begin{array}{cc} K^b_{AA}(\varepsilon) & K^b_{AI}(\varepsilon)\\ K^b_{IA}(\varepsilon) & K^b_{II}(\varepsilon)\end{array}\right\}\left\{\begin{array}{cc} G^b_{AA}(\varepsilon) & G^b_{AI}(\varepsilon)\\ G^b_{IA}(\varepsilon) & G^b_{II}(\varepsilon)\end{array}\right\}=\left\{\begin{array}{cc}1 & 0\\ 0 & 1\end{array}\right\},$$

$$G^b_{AA}(\varepsilon) = \left[K^b_{AA}(\varepsilon) - K^b_{AI}(\varepsilon)\, K^b_{II}(\varepsilon)^{-1} K^b_{IA}(\varepsilon)\right]^{-1} \quad (1)$$
$$G^b_{IA}(\varepsilon) = -K^b_{II}(\varepsilon)^{-1} K^b_{IA}(\varepsilon)\, G^b_{AA}(\varepsilon)$$

$$\left\{ \begin{array}{cc} K^a_{AA}(\varepsilon) & K^a_{AI}(\varepsilon) \\ K^a_{IA}(\varepsilon) & \infty \end{array} \right\} \left\{ \begin{array}{cc} G^a_{AA}(\varepsilon) & G^a_{AI}(\varepsilon) \\ G^a_{IA}(\varepsilon) & G^a_{II}(\varepsilon) \end{array} \right\} = \left\{ \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right\},$$

$$G^a_{IA}(\varepsilon) = G^a_{AI}(\varepsilon) = G^a_{II}(\varepsilon) = 0, \quad G^a_{AA}(\varepsilon) = K^a_{AA}(\varepsilon)^{-1} = G^a(\varepsilon)$$

$$\phi^a_A(\varepsilon, \mathbf{r})\, K^a_{AA}(\varepsilon)^{-1} = \left[\phi^b_A(\varepsilon, \mathbf{r}) - \phi^b_I(\varepsilon, \mathbf{r})\, K^b_{II}(\varepsilon)^{-1} K^b_{IA}(\varepsilon)\right] G^b_{AA}(\varepsilon) \quad (2)$$

which yields the *up-folding* of $\phi^a_A(\varepsilon, \mathbf{r})$ and the *downfolding* to $K^a_{AA}(\varepsilon)$: Since b is a strongly screened (tight-binding) representation, we start by generating $S^b(\varepsilon)$ through inversion of $[S(\varepsilon) + \kappa \cot\beta(\varepsilon)]_{BB}$ for a real-space cluster. For a crystal, we may Bloch sum to $S^\beta(\varepsilon, \mathbf{k})$ and add $\kappa \cot\eta^\beta(\varepsilon)$ in the diagonal to get $K^\beta(\varepsilon, \mathbf{k})$. *Downfolding* to $K^a_{AA}(\varepsilon)$ is given by (2) and (1). After finding the eigenvalues and eigenvectors

in the a-representation using e.g. the NMTO method, we *upfold* the wavefunction, charge density, or Green function using (2).

The screening transformation for the *Green matrix*, $G^\alpha(\varepsilon)$, is simply:

$$G^\alpha(\varepsilon) = \left[1 - \frac{\tan\alpha(\varepsilon)}{\tan\eta(\varepsilon)}\right] G(\varepsilon) \left[1 - \frac{\tan\alpha(\varepsilon)}{\tan\eta(\varepsilon)}\right] + \frac{\tan\alpha(\varepsilon)}{\kappa} \left[1 - \frac{\tan\alpha(\varepsilon)}{\tan\eta(\varepsilon)}\right]$$

which involves *no* matrix operations. Similarly, re-screening from β to α :

$$G^\alpha(\varepsilon) = \frac{\tan\eta^\alpha(\varepsilon)}{\tan\eta^\beta(\varepsilon)} G^\beta(\varepsilon) \frac{\tan\eta^\alpha(\varepsilon)}{\tan\eta^\beta(\varepsilon)} - \frac{\tan\beta(\varepsilon) - \tan\alpha(\varepsilon)}{\kappa} \frac{\tan\eta^\alpha(\varepsilon)}{\tan\eta^\beta(\varepsilon)}$$

which is the socalled *scaling relation*. Note that this formalism has been carried out assuming finite matrices. For infinite systems, they should therefore only be used in the $\mathbf{k}$-representation, unless due consideration is given.

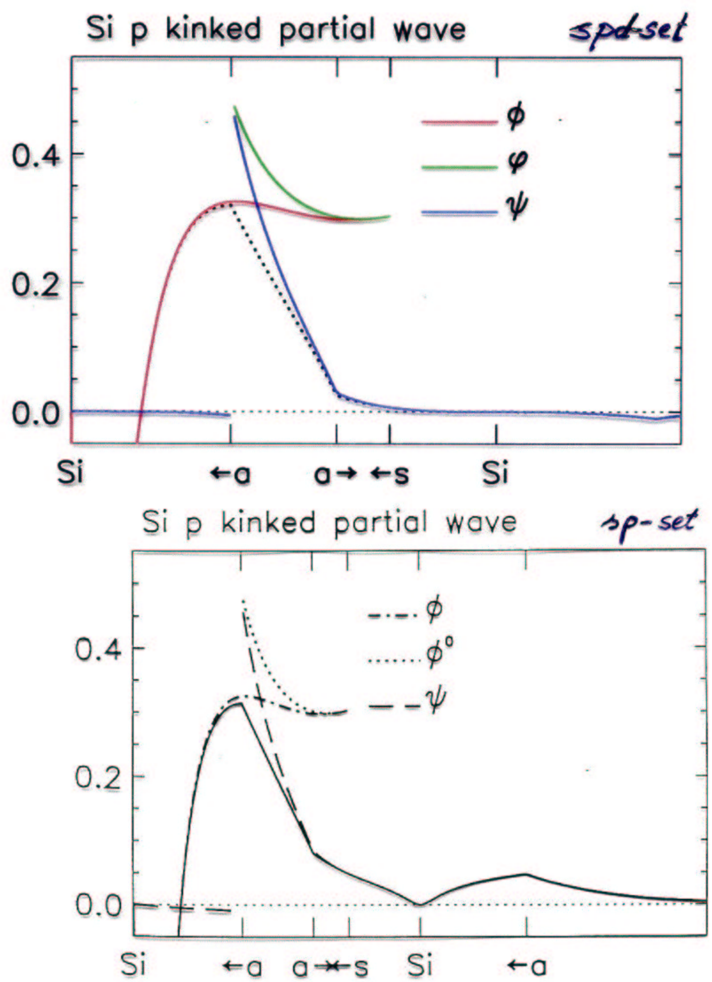
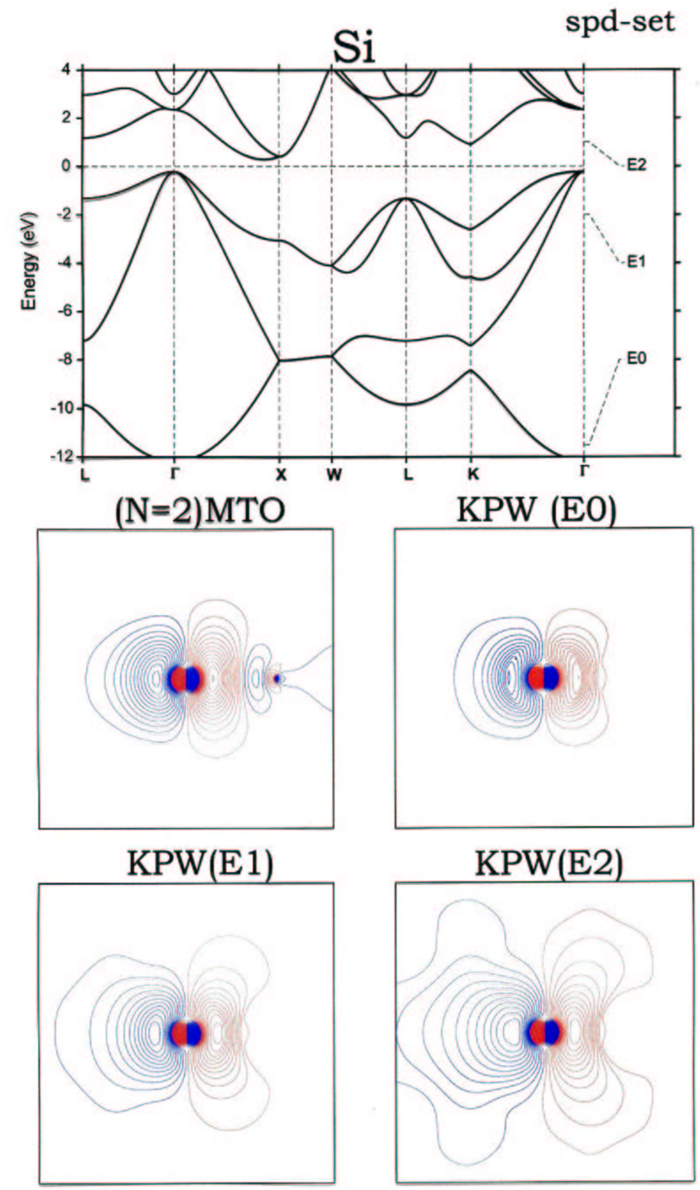
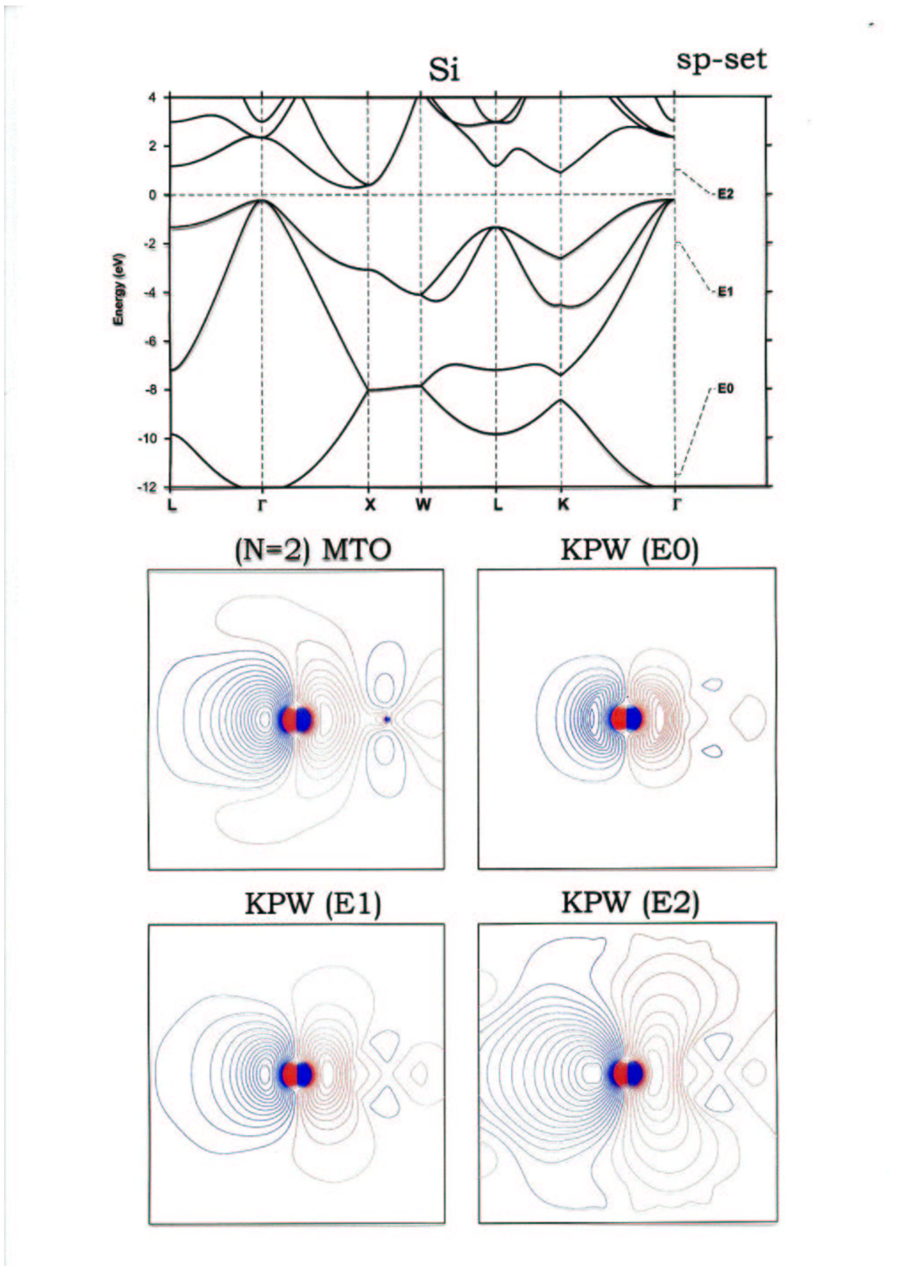
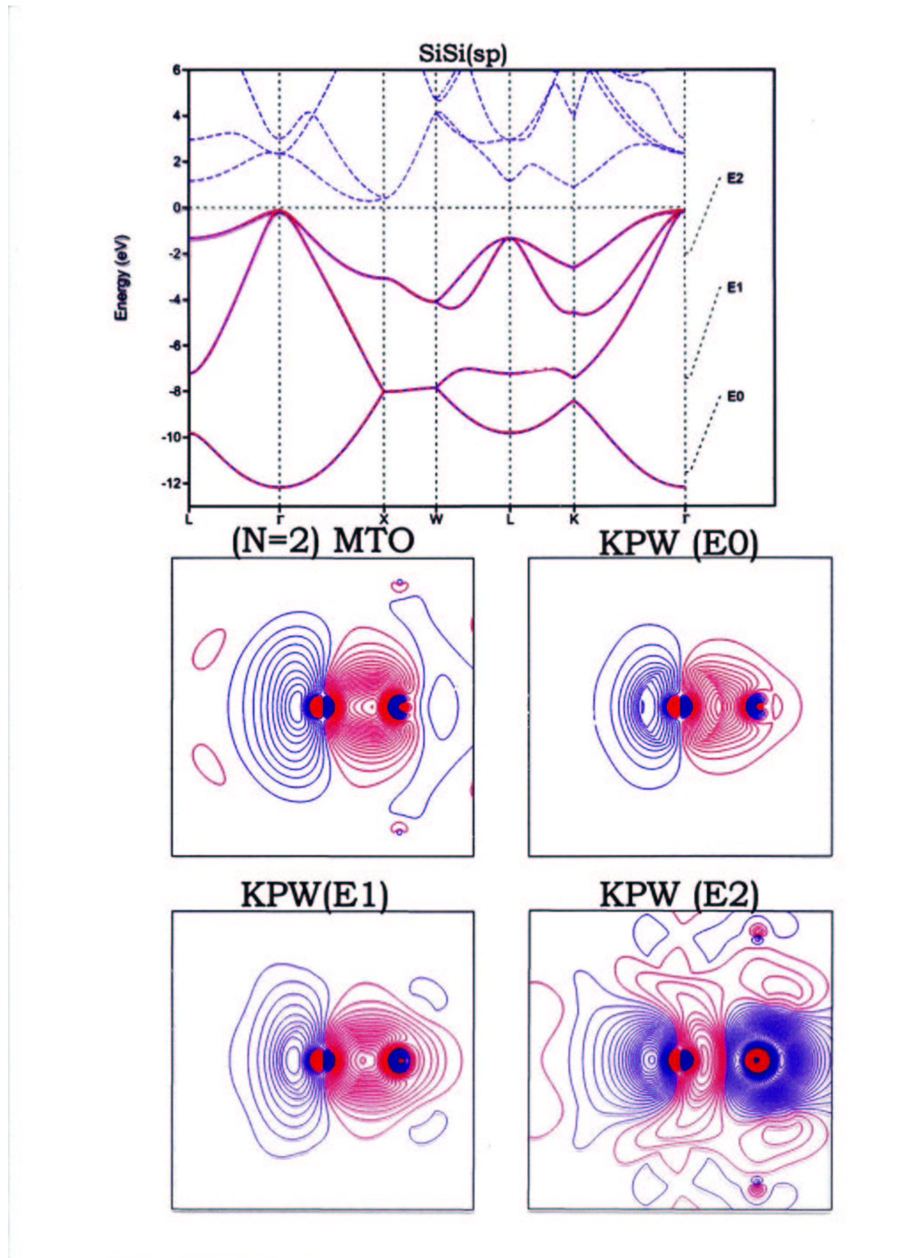
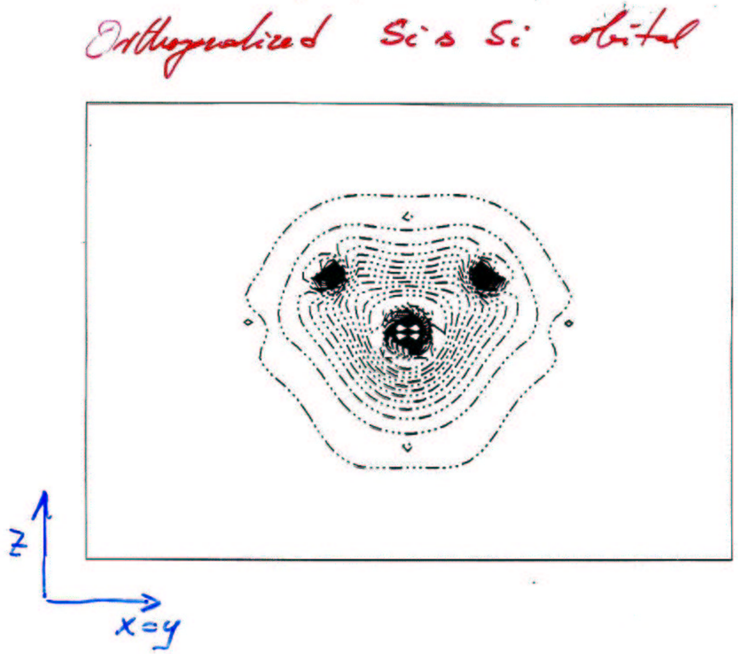


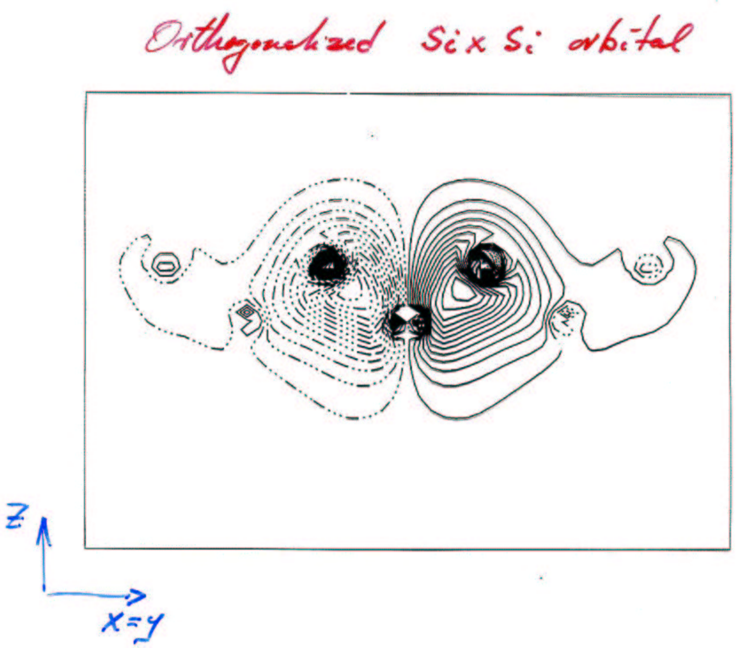
Fig. 4. Si p_{111} member of a screened minimal *sp*-set



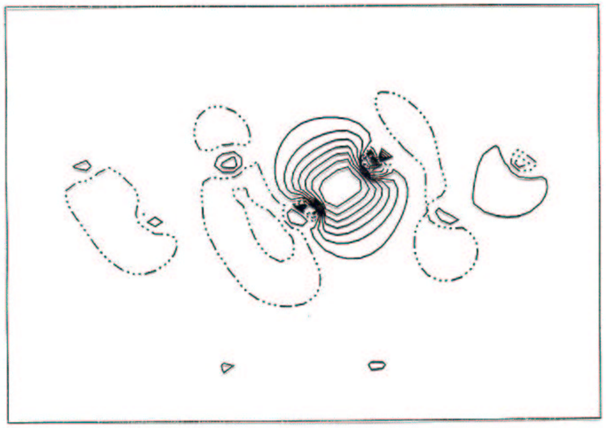

Si
sp-set
Energy (eV)
E2
E1
E0
L
Γ
X
W
L
K
Γ
(N=2) MTO
KPW (E0)
KPW (E1)
KPW (E2)


SiSi(sp)
Energy (eV)
E2
E1
E0
(N=2) MTO
KPW (E0)
KPW(E1)
KPW (E2)


Orthogonalized Si s Si orbital
z
x=y


Orthogonalized Si x Si orbital
z
x=y

Orthonormalize the (Si1$_s$, Si1$_x$, Si1$_y$, Si$_z$)-NMTO set and form Si1 sp^3 directed orbitals:

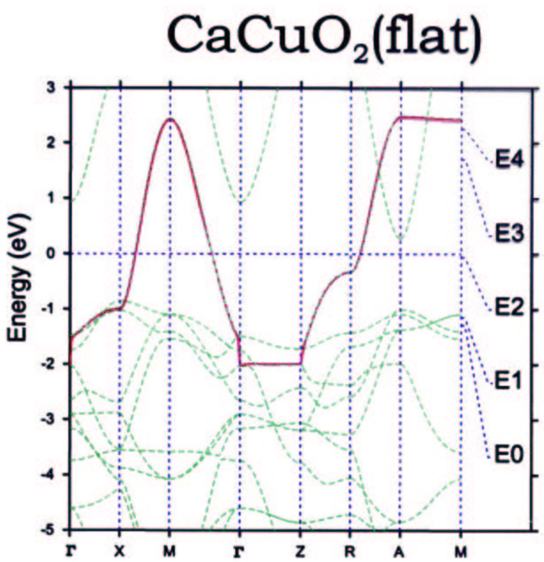


This converges to the bond orbital, if the energy mesh is made finer!

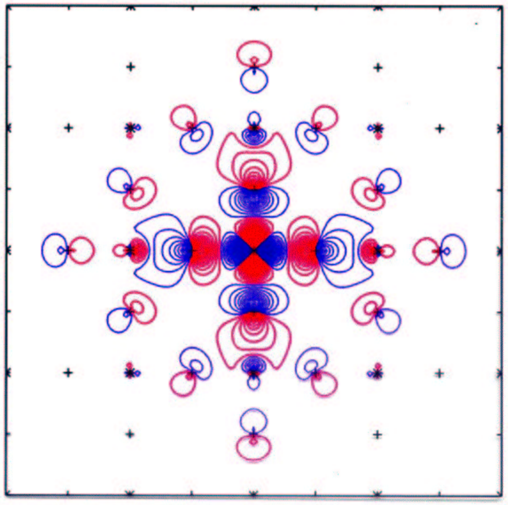
⇒ Direct generation of Wannier-like orbitals.

For the occupied states in band insulators, put the orbitals where the electrons are thought to be.

⇒ Order-N method.



(N=4) MTO



NMTOs

Given an energy mesh, $\epsilon_0, \epsilon_1, ..., \epsilon_N$,

can we generate a basis set, $\chi^{(N)}(\mathbf{r})$, with the property

that it spans the solutions of Schrödingers equation, $\Psi_i(\mathbf{r})$,

to within errors $\propto (\varepsilon_i - \epsilon_0)(\varepsilon_i - \epsilon_1) .... (\varepsilon_i - \epsilon_N)$?

$$\chi^{(N)}_{R'L'}(\mathbf{r}) = \sum_{n=0}^{N} \sum_{RL} \phi_{RL}(\epsilon_n, \mathbf{r}) \; L^{(N)}_{nRL,R'L'}$$

Andersen and Saha-Dasgupta, Phys Rev B62 R16219 (2000)

$$(\mathcal{H} - \varepsilon)\, \phi^a_{R'L'}(\varepsilon, \mathbf{r}) \;=\; -\sum_{RL} \delta(r_R - a_{RL})\, Y_L(\hat{\mathbf{r}}_R)\, K^a_{RL,R'L'}(\varepsilon)$$

$$(\mathcal{H} - \varepsilon) \sum_{R'L'} \phi^a_{R'L'}(\varepsilon, \mathbf{r})\, G^a_{R'L',RL}(\varepsilon) \;=\; -\delta(r_R - a_{RL})\, Y_L(\hat{\mathbf{r}}_R)$$

$$(\mathcal{H}_{\mathbf{r}} - \varepsilon)\, G\left(\varepsilon; \mathbf{r}, \mathbf{r}'\right) \;=\; -\delta\left(\mathbf{r} - \mathbf{r}'\right)$$

$$\phi(\varepsilon, \mathbf{r})\, G(\varepsilon) - \underbrace{\sum_{n=0}^{N} \phi(\epsilon_n, \mathbf{r})\, G(\epsilon_n)\, A^{(N)}_n(\varepsilon)}_{\text{analytical fct of } \varepsilon} \;\equiv\; \chi^{(N)}(\varepsilon, \mathbf{r})\, G(\varepsilon)$$

$$\phi(\varepsilon,\mathbf{r})\,G(\varepsilon)-\sum_{n=0}^{N}\phi(\epsilon_n,\mathbf{r})\,G(\epsilon_n)\,A_n^{(N)}(\varepsilon)\;\equiv\;\chi^{(N)}(\varepsilon,\mathbf{r})\,G(\varepsilon)$$

$$\begin{aligned}Want:\;\chi^{(N)}(\epsilon_0,\mathbf{r}) &= \chi^{(N)}(\epsilon_1,\mathbf{r}) = \;\ldots\; = \chi^{(N)}(\epsilon_N,\mathbf{r})\\ A_n^{(N)}(\varepsilon) &= polynomium\;\;of\;\;degree\quad N-1\end{aligned}$$

$$\frac{\Delta^N\phi(\mathbf{r})\,G}{\Delta[0...N]}-0=\frac{\Delta^N\chi^{(N)}(\mathbf{r})\,G}{\Delta[0...N]}=\chi^{(N)}(\mathbf{r})\,\frac{\Delta^N G}{\Delta[0...N]},$$

$$\chi^{(N)}(\mathbf{r})=\frac{\Delta^N\phi(\mathbf{r})\,G}{\Delta[0...N]}\left(\frac{\Delta^N G}{\Delta[0...N]}\right)^{-1}\to\left.\frac{d^N\phi(\varepsilon,\mathbf{r})\,G(\varepsilon)}{d\varepsilon^N}\right|_{\varepsilon_\nu}\left(\left.\frac{d^N G(\varepsilon)}{d\varepsilon^N}\right|_{\varepsilon_\nu}\right)^{-1}$$

$$\chi^{(N)}(\mathbf{r})=\sum_{n=0}^{N}\frac{\phi_n(\mathbf{r})\;G_n}{\prod_{m=0,\neq n}^{N}(\varepsilon_n-\varepsilon_m)}\left(\frac{\Delta^N G}{\Delta[0...N]}\right)^{-1}\equiv\sum_{n=0}^{N}\phi_n(\mathbf{r})\,L_n^{(N)},$$

$$\begin{aligned}\chi^{(N)}(\mathbf{r}) &= \phi(\epsilon_N,\mathbf{r})+\frac{\Delta\phi(\mathbf{r})}{\Delta[N-1,N]}\left(E^{(N)}-\epsilon_N\right)+..\\ &\quad ..+\frac{\Delta^N\phi(\mathbf{r})}{\Delta[0...N]}\left(E^{(1)}-\epsilon_1\right)..\left(E^{(N)}-\epsilon_N\right),\end{aligned}$$

$$\begin{aligned}\phi^{(N)}(\varepsilon,\mathbf{r}) &= \phi(\epsilon_N,\mathbf{r})+\frac{\Delta\phi(\mathbf{r})}{\Delta[N-1,N]}(\varepsilon-\epsilon_N)+..\\ &\quad ..+\frac{\Delta^N\phi(\mathbf{r})}{\Delta[0...N]}(\varepsilon-\epsilon_1)..(\varepsilon-\epsilon_N),\end{aligned}$$

The MTO set is a polynomial approximation to the energy dependence of the set of kinked partial waves, in 'quantized' form.

$$(\mathcal{H}-\varepsilon_N)\,\chi^{(N)}(\mathbf{r}) \;=\; \chi^{(N-1)}(\mathbf{r})\left(E^{(N)}-\varepsilon_N\right)$$

$$E^{(M)}=\left(\frac{\Delta^M \varepsilon G}{\Delta\,[0..M]}\right)\left(\frac{\Delta^M G}{\Delta\,[0..M]}\right)^{-1}$$

Hamiltonian and overlap matrices from:

$$\frac{\Delta^N G}{\Delta\,[0...N]}\left\langle \chi^{(N)}\,|\varepsilon-\mathcal{H}|\,\chi^{(N)}\right\rangle\frac{\Delta^N G}{\Delta\,[0...N]}=$$

$$\frac{\Delta^{2N} G}{\Delta\,[[0..N-1]\,N]}+(\varepsilon-\epsilon_N)\,\frac{\Delta^{2N+1} G}{\Delta\,[[0...N]]}$$

We may transform to (nearly) orthonormal sets:

$$\left\langle \hat{\chi}^{(M-1)}\mid\hat{\chi}^{(M)}\right\rangle \;\equiv\; \left\langle \hat{\chi}^{(L)}\mid\hat{\chi}^{(L)}\right\rangle \;\equiv 1$$

for all $1 \leq M \leq N$ and one L.

In such a representation, the energy matrices are Hermitian:

$$\hat{E}^{(M)}-\varepsilon_M \;=\; \left\langle \hat{\chi}^{(M)}\,|\mathcal{H}-\varepsilon_M|\,\hat{\chi}^{(M)}\right\rangle,$$

We have derived useful, minimal sets of short-ranged orbitals from scattering theory.

Into a calculation enters:

(1) The phase shifts of the potential wells.
(2) A choice of which orbitals to include in the set, *i.e.* the active channels.
(3) For these, a choice of screening radii, a_{RL}, to control the orbital ranges.
(4) An energy mesh on which the set will provide exact solutions.

These MTOs have significant advantages over those used in the past.