Tight-Binding Models and Coulomb Interactions for s, p and d Electrons

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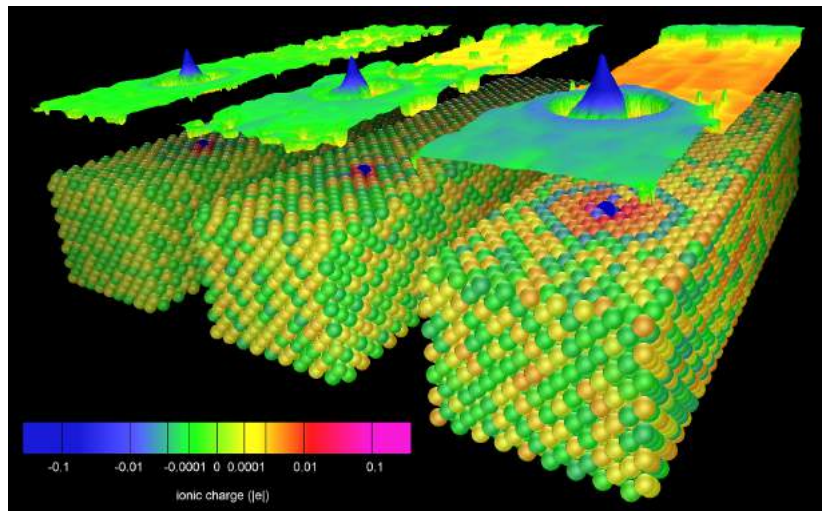
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Autumn School on Correlated Electrons

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Outline

ionic charge (|e|)

The Schrödinger equation

Understanding the behaviour of electrons in solids almost always requires us to solve the Schrödinger equation:

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$$

- $V_{\text{eff}}(\boldsymbol{r})$ depends on the approximations being used.
- If $\boldsymbol{r}$ means $(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, this is the N-electron Schrödinger equation.
- Most of the methods used are based on the variational principle.

Variational formulation of the Schrödinger equation

Solving the Schrödinger equation

$$\hat{H}\psi_i = \epsilon_i \psi_i$$

to find the eigenvalues and eigenfunctions of $\hat{H}$ is equivalent to finding the stationary points of the functional

$$\epsilon[\psi] = \langle \psi | \hat{H} | \psi \rangle$$

subject to the normalization constraint

$$\langle \psi | \psi \rangle = 1$$

Practical importance of the variational formulation

- Suppose $\tilde{\psi}_i$ is a normalized guess at ψ_i with error $\Delta\psi_i$.
- Since $\epsilon[\psi]$ is stationary and equal to ϵ_i when $\psi = \psi_i$,

$$\epsilon[\tilde{\psi}_i] = \epsilon_i + \mathcal{O}[(\Delta\psi_i)^2]$$

- If $\tilde{\psi}_i$ is accurate, $\tilde{\epsilon}_i$ is even more accurate.

This simple observation underlies the success of almost all current methods used to solve the Schrödinger equation

The linear variational principle

A convenient way to guess solutions is to use a basis set

$$\tilde{\psi}(\boldsymbol{c}, \boldsymbol{r}) = \sum_{\alpha=1}^{M} c_\alpha \phi_\alpha(\boldsymbol{r})$$

and choose c_α to make

$$\epsilon[\tilde{\psi}] = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle = \sum_{\alpha,\beta}^{M} c_\alpha^* \langle \phi_\alpha | \hat{H} | \phi_\beta \rangle c_\beta$$

stationary subject to

$$\langle \tilde{\psi} | \tilde{\psi} \rangle = \sum_{\alpha,\beta}^{M} c_\alpha^* \langle \phi_\alpha | \phi_\beta \rangle c_\beta = 1$$

- Defining the Hamiltonian and overlap matrices

$$H_{\alpha\beta} = \int \phi_\alpha^*(\boldsymbol{r})\hat{H}\phi_\beta(\boldsymbol{r})d^3r, \qquad S_{\alpha\beta} = \int \phi_\alpha^*(\boldsymbol{r})\phi_\beta(\boldsymbol{r})d^3r,$$

  we seek the stationary points of

$$\epsilon(\boldsymbol{c}) = c_\alpha^* H_{\alpha\beta} c_\beta \qquad \text{(summation convention)}$$

  subject to $c_\alpha^* S_{\alpha\beta} c_\beta = 1$.

- Not surprisingly, this is equivalent to solving the matrix Schrödinger equation

$$H_{\alpha\beta} c_\beta = \tilde{\epsilon} S_{\alpha\beta} c_\alpha$$

Advantages and disadvantages

$$H_{\alpha\beta}\boldsymbol{c}_\beta = \tilde{\epsilon}S_{\alpha\beta}\boldsymbol{c}_\alpha$$

Advantages

- Solving the matrix problem yields M approximate eigenvalues $\tilde{\epsilon}_i$ and eigenvectors $\boldsymbol{c}_i$ at once.
- Solving matrix eigenvalue problems is much easier than finding the eigenfunctions and eigenvalues of differential equations. Excellent general purpose numerical libraries are available.

Disadvantages

- Calculating $H_{\alpha\beta}$ and $S_{\alpha\beta}$ can be painful.
- Diagonalizing very large matrices is slow.

The Rayleigh-Ritz variational principle

If $\tilde{\psi}_0, \tilde{\psi}_1, \ldots, \tilde{\psi}_{M-1}$ are the *M* approximate eigenfunctions obtained by solving a linear variational problem with *M* basis functions, then

$$\tilde{\epsilon}_i = \langle \tilde{\psi}_i | \hat{H} | \tilde{\psi}_i \rangle \geq \epsilon_i, \qquad i = 0, 1, \ldots, M-1$$

- Every eigenvalue obeys a variational principle.
- Improving the basis set can only lower the approximate eigenvalues.
- The convergence with basis set is reassuringly controlled.
- Errors of order $\Delta\psi_i$ in $\tilde{\psi}_i$ lead to errors of order $(\Delta\psi_i)^2$ in $\tilde{\epsilon}_i$.

Siloxane on Silica
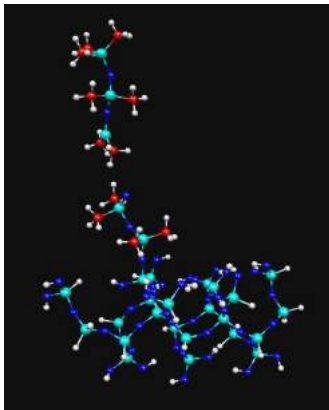
A quantum MD simulation of the tearing of a siloxane molecule from a silica surface

What is tight binding?

> TB $\equiv$ Linear variational approach with atomic-like orbitals

Most natural when orbitals overlap little and bands are narrow.

Three flavours:

- Ab initio
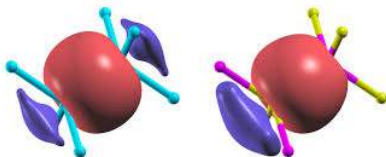- Wannier-function-based
- Semi-empirical

Ab initio tight binding

- Explicit basis of Gaussians, Slater-type or atomic-like orbitals. Not usually orthogonal.

- Evaluate matrix elements computationally.

- Solve matrix eigenvalue problem computationally.

- Similar in style to conventional quantum chemical approaches.
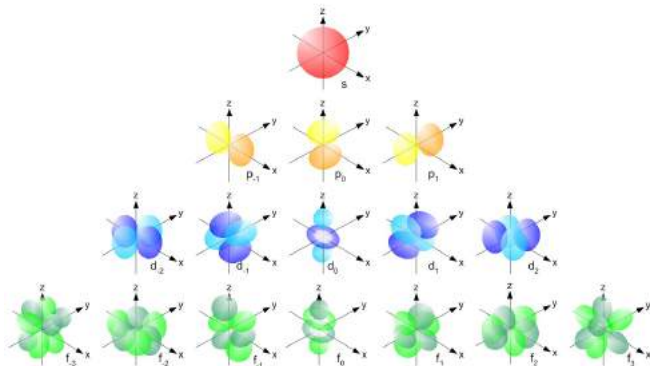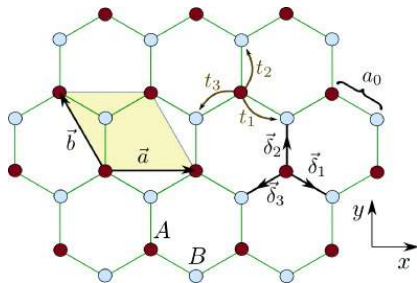
Wannier-function-based tight binding

- Orthogonal or non-orthogonal localized linear combinations of Bloch eigenfunctions.

- By construction span the bands from which they were created exactly.

- Calculating Wannier functions requires solving the Schrödinger equation.

- Complicated form $\Rightarrow$ no simple parameterization.

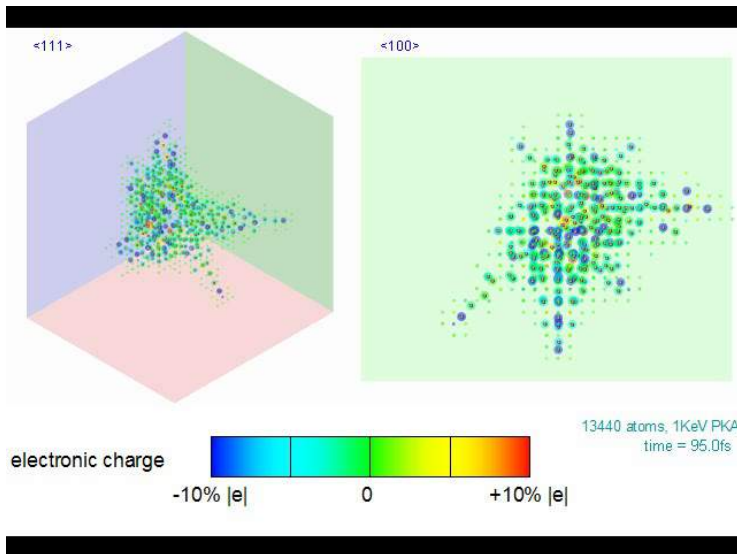Maximally localized bonding Wannier functions constructed from the four valence bands of Si (left) and GaAs (right)

Semi-empirical tight binding

- No explicit orbitals. Instead parameterize matrix elements.

- Orthogonal or non-orthogonal.

- Minimal basis. Quick to set up and solve.

- Analytically tractable in simple cases.

- Inaccurate. Unreliable. Non-transferable.

- Best for qualitative information.

Semi-empirical tight binding: cascade simulation

electronic charge

-10% |e| 0   +10% |e|

13440 atoms, 1KeV PKA
time = 95.0fs

$$V_{\text{eff}}(\boldsymbol{r}) = \sum_I V_I(\boldsymbol{r} - \boldsymbol{R}_I)$$

| $sp\sigma$ | zero | $pd\sigma$ | $pd\pi$ | zero |
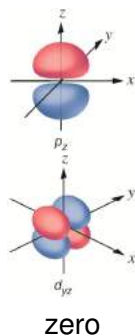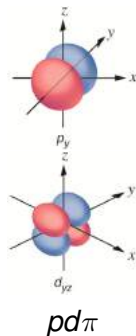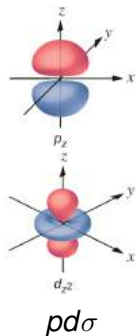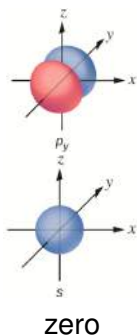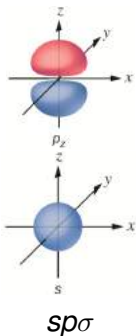
Slater-Koster rules
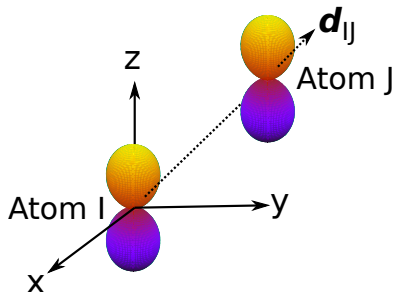
This matrix element is neither $H_{pp\sigma}$ or $H_{pp\pi}$, but since

$$\hat{R}\Big) Y_l^m = \sum_{m'=-l}^{l} D_{m',m}^l(\omega)\, Y_l^{m'}$$

it can be expressed in terms of them.

Example: bandstructure of a face-centred cubic solid
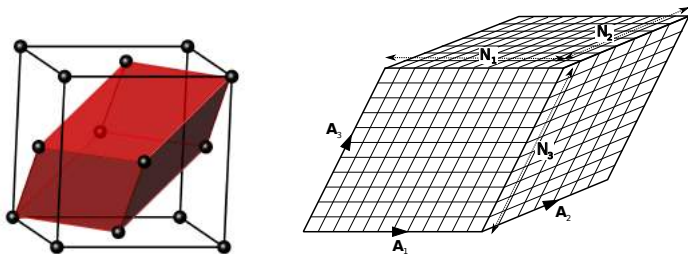
- For an FCC crystal

$$\boldsymbol{A}_1 = \frac{a}{2}(0,1,1), \qquad \boldsymbol{A}_2 = \frac{a}{2}(1,0,1), \qquad \boldsymbol{A}_3 = \frac{a}{2}(1,1,0),$$

$$\boldsymbol{B}_1 = \frac{2\pi}{a}(-1,1,1), \quad \boldsymbol{B}_2 = \frac{2\pi}{a}(1,-1,1), \quad \boldsymbol{B}_3 = \frac{2\pi}{a}(1,1,-1).$$

- The $N_1 N_2 N_3$ distinct $\boldsymbol{k}$ vectors consistent with the periodic boundary conditions are

$$\boldsymbol{k} = \frac{m_1}{N_1}\boldsymbol{B}_1 + \frac{m_2}{N_2}\boldsymbol{B}_2 + \frac{m_3}{N_3}\boldsymbol{B}_3, \qquad 0 \le m_i < N_i.$$

- Orthogonal tight-binding model with one *s* orbital per atom.
- Diagonal matrix elements are 0 and nearest-neighbour hopping matrix element are *h*. All other matrix elements are zero.

Bloch's theorem says that the tight-binding eigenfunctions take the form

$$|\psi_{\boldsymbol{k}}\rangle = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}} |\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}}$$

- Applying the TB Hamiltonian $\hat{H}^{\text{TB}} = \sum_{\boldsymbol{d}, \boldsymbol{d}'} |\phi_{\boldsymbol{d}}\rangle H_{\boldsymbol{d}, \boldsymbol{d}'} \langle \phi_{\boldsymbol{d}'}|$ to the Bloch linear combination gives

$$
\begin{aligned}
\hat{H}^{\text{TB}}|\psi_{\boldsymbol{k}}\rangle &= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}} \hat{H}^{\text{TB}}|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}} \\
&= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} \sum_{\boldsymbol{d}} |\phi_{\boldsymbol{d}'}\rangle \langle \phi_{\boldsymbol{d}'}|\hat{H}^{\text{TB}}|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}} \\
&= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} |\phi_{\boldsymbol{d}'}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}'} \sum_{\boldsymbol{d}} \langle \phi_{\boldsymbol{d}'}|\hat{H}^{\text{TB}}|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot(\boldsymbol{d}-\boldsymbol{d}')}.
\end{aligned}
$$

- The only non-zero contributions to the inner summation are those for which $\boldsymbol{d}$ is a nearest neighbour of $\boldsymbol{d}'$.

$$\hat{H}^{\text{TB}}|\psi_{\boldsymbol{k}}\rangle = \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} |\phi_{\boldsymbol{d}'}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}'} \sum_{\boldsymbol{d}} \langle\phi_{\boldsymbol{d}'}|\hat{H}^{\text{TB}}|\phi_{\boldsymbol{d}}\rangle e^{i\boldsymbol{k}\cdot(\boldsymbol{d}-\boldsymbol{d}')}$$

$$= \frac{1}{\sqrt{N_1 N_2 N_3}} \sum_{\boldsymbol{d}'} |\phi_{\boldsymbol{d}'}\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{d}'} \sum_{\boldsymbol{n}} h e^{i\boldsymbol{k}\cdot\boldsymbol{n}}$$

$$= \left(h \sum_{\boldsymbol{n}} e^{i\boldsymbol{k}\cdot\boldsymbol{n}} \right) |\psi_{\boldsymbol{k}}\rangle$$

The sum over nearest-neighbour vectors $\boldsymbol{n}$ is easily evaluated to obtain the bandstructure:

$$\epsilon(\boldsymbol{k}) = 4h \left[\cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right) \cos\left(\frac{k_x a}{2}\right) \right.$$
$$\left. + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \right]$$

(You do not often you get to calculate a bandstructure by hand in a few lines!)

TB total energies
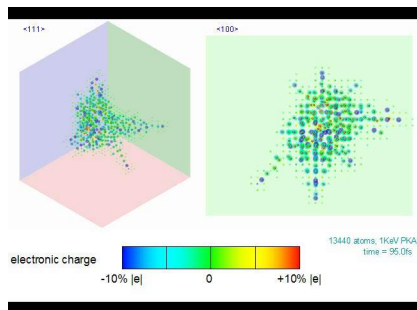
TB total energy expression

$$E_{\text{total}}^{\text{TB}}(\boldsymbol{d}) = \sum_{i \text{ occ}} \epsilon_i(\boldsymbol{d}) + \sum_{I>J} V_{\text{ion-ion}}^{\text{pair}}(\boldsymbol{d}_I - \boldsymbol{d}_J)$$

All matrix elements and inter-atomic potentials need to be fitted.

. . . is a black art.

- Bandstructures or total energies?
- Lots of data or a little?
- Transferability?

TB total energy model for silicon

$$h_\alpha(r) = h_\alpha(r_0) \left(\frac{r_0}{r}\right)^n f_c(r)$$

$$V_{\text{ion-ion}}^{\text{pair}}(r) = V_{\text{ion-ion}}^{\text{pair}}(r_0) \left(\frac{r_0}{r}\right)^m f_c(r)$$

Parameter	Value (eV)
E_s	-6.535
E_p	1.760
$h_{ss\sigma}(r_0)$	-1.820
$h_{sp\sigma}(r_0)$	1.960
$h_{pp\sigma}(r_0)$	3.060
$h_{pp\pi}(r_0)$	-0.870
$V_{\text{ion-ion}}^{\text{pair}}(r_0)$	3.458

Parameter	Value
r_0	2.360Å
n	2
m	4.54
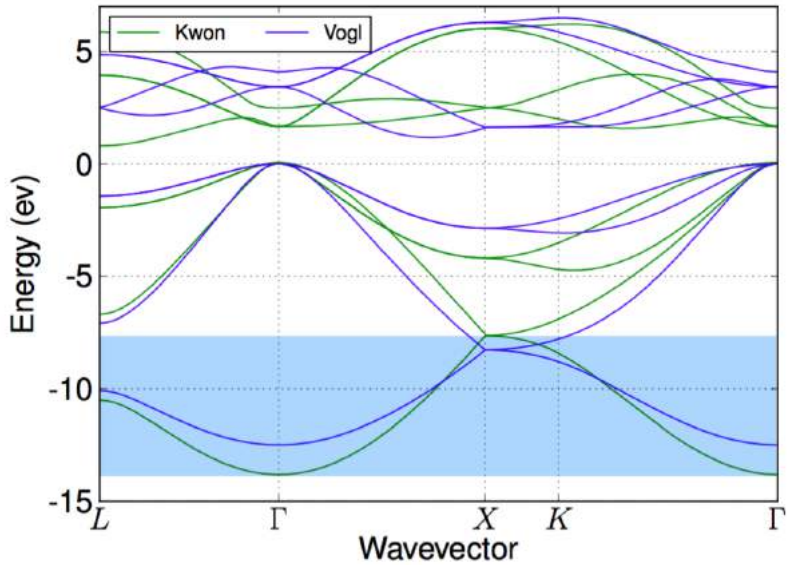
Electron Elevator
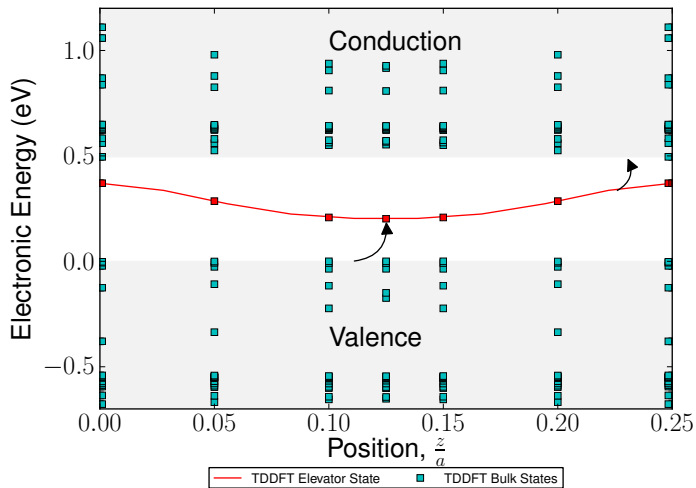
Elevator Effect
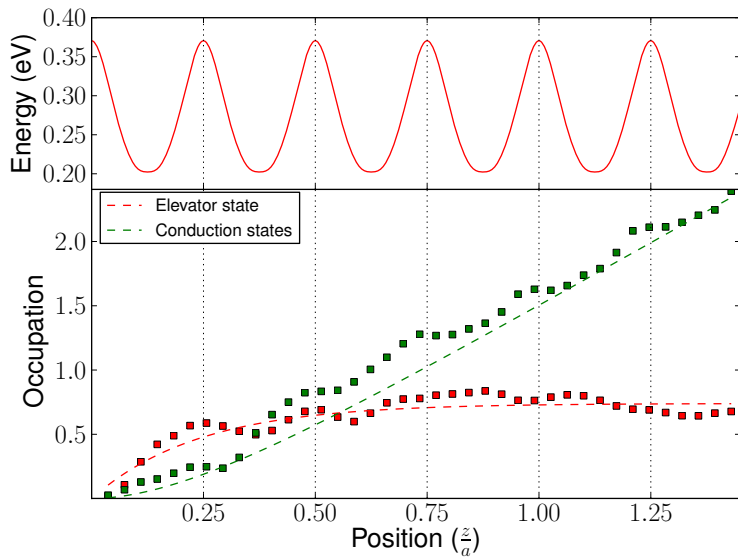
The central problem of condensed matter physics

The many-electron Schrödinger equation

$$\left(-\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_I \frac{Z_I\, e^2}{|\mathbf{r}_i - \mathbf{d}_I|} + \sum_{I>J} \frac{Z_I Z_J\, e^2}{|\mathbf{d}_I - \mathbf{d}_J|} \right) \Psi = E\Psi$$

is our grand unified theory.

$$\left(\hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} + E_{\text{nn}} \right) \Psi = E\Psi$$

If only we could solve it!

The energy functional

There exists a functional $E[n]$ which is minimized and equal to the ground-state energy E_0 when the electron density $n(\boldsymbol{r})$ is equal to the ground-state electron density $n_0(\boldsymbol{r})$.

The Levy construction

$$E[n] = \text{Min}_{\Psi \to n(\boldsymbol{r})} \langle \Psi | \hat{H} | \Psi \rangle$$

Terms in $E[n]$

$$E[n] = T_s[n] + E_{en}[n] + E_H[n] + E_{nn} + E_{xc}[n]$$

- $T_s[n]$ is the KE of a system of non-interacting electrons with ground-state electron density $n(\boldsymbol{r})$

- $E_{en}[n] = \displaystyle\int V_{nuc}(\boldsymbol{r})n(\boldsymbol{r})d^3r$

- $E_H[n] = \dfrac{1}{2}\displaystyle\iint \dfrac{e^2 n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3r d^3r'$

- $E_{xc}[n]$ is known as the exchange-correlation energy

Self-consistency

The Euler-Lagrange equation derived by minimizing $E[n]$ looks like a non-interacting Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}([n], \boldsymbol{r})\right)\psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r})$$

except that

$$V_{KS}([n], \boldsymbol{r}) = V_{nuc}(\boldsymbol{r}) + \underbrace{\int \frac{e^2 n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r'}_{\text{Hartree potential}} + \underbrace{\frac{\delta E_{xc}}{\delta n(\boldsymbol{r})}}_{V_{xc}([n], \boldsymbol{r})}$$

depends on the electron density $n(\boldsymbol{r}) = \sum_{i \text{ occ}} |\psi_i(\boldsymbol{r})|^2$.

An iterative method of solution is required

Self-consistent total energy

Once self-consistency has been reached the total energy is obtained using

$$E[n] = T_s[n] + E_{en}[n] + E_H[n] + E_{nn} + E_{xc}[n]$$

with

$$n(\mathbf{r}) = \sum_{i \text{ occ}} |\psi_i(\mathbf{r})|^2$$

and

$$T_s[n] = \sum_{i \text{ occ}} \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d^3 r$$

Since

$$T_s[n] = \sum_{i \text{ occ}} \int \psi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_i(\boldsymbol{r}) d^3r$$

$$= \sum_{i \text{ occ}} \int \psi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{KS}}([n], \boldsymbol{r}) - V_{\text{KS}}([n], \boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) d^3r$$

$$= \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{KS}}([n], \boldsymbol{r}) n(\boldsymbol{r}) d^3r$$

the total energy can also be expressed as

$$E[n] = \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{KS}}[n]n + E_{\text{en}}[n] + E_{\text{H}}[n] + E_{\text{nn}} + E_{\text{xc}}[n]$$

Comparison of DFT and TB total energies

DFT

$$E[n] = \sum_{i \text{ occ}} \epsilon_i - \int V_{\text{KS}} n + E_{\text{en}}[n] + E_{\text{H}}[n] + E_{\text{nn}} + E_{\text{xc}}[n]$$

TB

$$E_{\text{total}}^{\text{TB}} = \sum_{i \text{ occ}} \epsilon_i + \sum_{I > J} V_{\text{ion-ion}}^{\text{pair}}(\boldsymbol{d}_I - \boldsymbol{d}_J)$$

- The TB Schrödinger equation is not self-consistent.
- The potential in the TB Schrödinger equation is normally assumed to be a sum of spherical atomic-like potentials.
- The TB double-counting term is simple and pairwise.

Variational TB

The non-selfconsistent tight-binding total energy is a stationary approximation to the DFT total energy.

General variational formulation of DFT

Consider the following functional of $n(\mathbf{r})$, $V_{\text{eff}}(\mathbf{r})$ and $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$

$$E[n, V_{\text{eff}}, \Psi] = \langle \Psi | \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + V_{\text{eff}}(\mathbf{r}_i) \right) | \Psi \rangle - \int V_{\text{eff}} n + G[n]$$

where

$$G[n] = \int V_{\text{nuc}} n + E_{\text{H}}[n] + E_{\text{xc}}[n] + E_{\text{nn}}$$

$$\frac{\delta G}{\delta n} = V_{\text{nuc}} + V_{\text{H}} + V_{\text{xc}} = V_{\text{KS}}$$

Euler-Lagrange equations

$$E[n, V_{\text{eff}}, \Psi] = \langle \Psi | \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + V_{\text{eff}}(\boldsymbol{r}_i) \right) | \Psi \rangle - \int V_{\text{eff}} n + G[n]$$

The corresponding Euler-Lagrange equations are fully equivalent to DFT!

$$\frac{\delta E}{\delta n} = -V_{\text{eff}} + \frac{\delta G}{\delta n} = -V_{\text{eff}} + V_{\text{KS}} = \mu$$

$$\frac{\delta E}{\delta V_{\text{eff}}} = \langle \Psi | \hat{n}(\boldsymbol{r}) | \Psi \rangle - n(\boldsymbol{r}) = 0$$

$$\frac{\delta E}{\delta \Psi^*} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + V_{\text{eff}}(\boldsymbol{r}_i) \right) | \Psi \rangle = E | \Psi \rangle$$

Note: the middle equation follows because

$$\langle \Psi | \sum_{i=1}^{N} V_{\text{eff}}(\boldsymbol{r}_i) | \Psi \rangle = \langle \Psi | \int \left(\sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \right) V_{\text{eff}}(\boldsymbol{r}) d^3 r | \Psi \rangle = \langle \Psi | \int \hat{n}(\boldsymbol{r}) V_{\text{eff}}(\boldsymbol{r}) d^3 r | \Psi \rangle$$

If we evaluate $E[n, V_{\text{eff}}, \Psi]$ for guessed inputs, the errors will be second order in

$$\Delta n = n - n_0, \qquad \Delta V_{\text{eff}} = V_{\text{eff}} - V_{\text{KS}}([n_0]), \qquad \Delta \Psi = \Psi - \Psi_0.$$

good guesses $\Rightarrow$ better energies

The Generalized Harris functional

The generalized formulation is rather too general, so specialize.

- Given choices for n and V_{eff}, minimize

$$E[n, V_{\text{eff}}, \Psi] = \langle \Psi | \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 + V_{\text{eff}}(\boldsymbol{r}_i) \right) | \Psi \rangle - \int V_{\text{eff}} n + G[n]$$

with respect to Ψ to obtain

$$E[n, V_{\text{eff}}] = \sum_{i \text{ occ}} \epsilon_i[V_{\text{eff}}] - \int V_{\text{eff}} n + G[n]$$

(Specializing further by setting $V_{\text{eff}}(\boldsymbol{r}) = V_{\text{KS}}([n], \boldsymbol{r})$
yields the Harris functional of $n(\boldsymbol{r})$ alone)

TB and the Harris functional

Non-selfconsistent Harris DFT total energy

$$E[n, V_{\text{eff}}] = \sum_{i \text{ occ}} \epsilon_i[V_{\text{eff}}] - \int V_{\text{eff}} n + G[n]$$

Tight binding total energy

$$E_{\text{total}}^{\text{TB}} = \sum_{i \text{ occ}} \epsilon_i + \sum_{I > J} V_{\text{ion-ion}}^{\text{pair}}(\boldsymbol{d}_I - \boldsymbol{d}_J)$$

If we set

$$n(\boldsymbol{r}) = \sum_I n_I(\boldsymbol{r} - \boldsymbol{d}_I) \qquad V(\boldsymbol{r}) = \sum_I V_I(\boldsymbol{r} - \boldsymbol{d}_I)$$

the two functionals are (almost) the same.

Effectiveness

TB models and DFT

The tight-binding total energy is a good approximation to the non-selfconsistent total energy of Harris DFT.

- The input density and potential are superpositions of spherical atomic- or ionic-like contributions.
  - Fails when the atomic configuration in the solid is very unlike that of an isolated atom (solution: smarter trial densities/potentials)
  - Problems with charge transfer (solution: self-consistent TB)

Bottom line

With a good basis set and good input densities/potentials, non-selfconsistent TB is quantitatively accurate.

Semi-empirical tight binding: dynamic screening

A point charge q moves at velocity $\boldsymbol{v}_0$ through a solid.
At high velocity (top panel), the electronic screening cloud
cannot keep up.
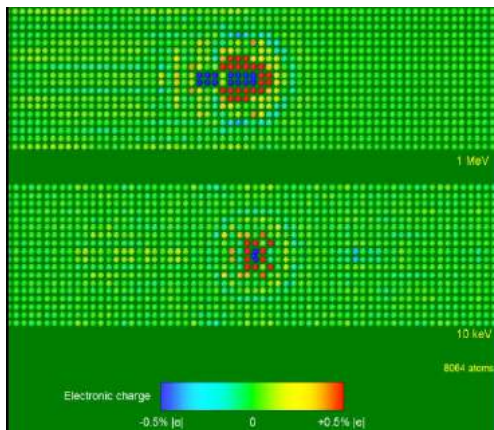
Many-electron tight-binding models

The many-electron equivalent of a TB model is:

$$\hat{H} = \sum_{\zeta} \sum_{\alpha\beta} \hat{c}^{\dagger}_{\alpha,\zeta} h_{\alpha\beta} \hat{c}_{\beta,\zeta} + \frac{1}{2} \sum_{\zeta,\zeta'} \sum_{\alpha\beta\gamma\delta} \hat{c}^{\dagger}_{\alpha,\zeta} \hat{c}^{\dagger}_{\beta,\zeta'} V_{\alpha\beta,\chi\gamma} \hat{c}_{\gamma,\zeta'} \hat{c}_{\chi,\zeta}$$

where $\hat{c}^{\dagger}_{\alpha,\zeta}$ is the creation operator for an atomic-like spin-orbital

$$\phi_{\alpha,\zeta}(\boldsymbol{r}, s) = \phi_{\alpha}(\boldsymbol{r}) \chi_{\zeta}(s)$$

The matrix elements are

$$h_{\alpha\beta} = \int \phi_{\alpha}^{*}(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\boldsymbol{r}) \right) \phi_{\beta}(\boldsymbol{r}) \, d^3 r$$

$$V_{\alpha\beta,\chi\gamma} = \iint \phi_{\alpha}^{*}(\boldsymbol{r}) \phi_{\beta}^{*}(\boldsymbol{r}') \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \phi_{\chi}(\boldsymbol{r}) \phi_{\gamma}(\boldsymbol{r}) \, d^3 r \, d^3 r'$$

Symmetry requirements

$$\hat{H} = \sum_{\zeta} \sum_{\alpha\beta} \hat{c}^{\dagger}_{\alpha,\zeta} h_{\alpha\beta} \hat{c}_{\beta,\zeta} + \frac{1}{2} \sum_{\zeta,\zeta'} \sum_{\alpha\beta\gamma\delta} \hat{c}^{\dagger}_{\alpha,\zeta} \hat{c}^{\dagger}_{\beta,\zeta'} V_{\alpha\beta,\chi\gamma} \hat{c}_{\gamma,\zeta'} \hat{c}_{\chi,\zeta}$$

- If $\phi_{\alpha}(\boldsymbol{r}) \propto Y_l^m(\hat{\boldsymbol{r}})$, the one-particle matrix elements $h_{\alpha\beta}$ can all be expressed in terms of a few numbers: $h_{ss\sigma}$, $h_{pd\pi}$, …
- Are there analogous simplifications for $V_{\alpha\beta,\chi\gamma}$?

What is the most general form of $V_{\alpha\beta,\chi\gamma}$ allowed by symmetry?

(The answer has been known since the time of Slater,
but people often get it wrong even today.)

For simplicity, consider a single angular momentum shell on a single atom.

- The $2l + 1$ spatial orbitals in the basis are

$$\phi_m(\boldsymbol{r}) = R_{nl}(r) Y_l^m(\hat{\boldsymbol{r}}), \qquad -l \leq m \leq l$$

- $V_{\alpha\beta,\chi\gamma}$ has $(2l + 1)^4$ elements.
- How many are independent?

Rotational symmetry

- The basis functions transform into linear combinations of each other under rotations:

$$\hat{R}^{\boldsymbol{\omega}} \phi_\alpha(\boldsymbol{r}) = \sum_{\alpha'=-l}^{l} D^l_{\alpha',\alpha}(\boldsymbol{\omega}) \phi_{\alpha'}(\boldsymbol{r})$$

- The Coulomb interaction $e^2/|\boldsymbol{r} - \boldsymbol{r}'|$ is unchanged if $\boldsymbol{r}$ and $\boldsymbol{r}'$ are rotated simultaneously.

- $\displaystyle V_{\alpha\beta,\chi\gamma} = \iint \phi^*_\alpha(\boldsymbol{r}) \phi^*_\beta(\boldsymbol{r}') \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \phi_\chi(\boldsymbol{r}) \phi_\gamma(\boldsymbol{r}') d^3r \, d^3r'$

$$= \iint \left(\hat{R}^{\boldsymbol{\omega}} \phi_\alpha(\boldsymbol{r})\right)^* \left(\hat{R}^{\boldsymbol{\omega}} \phi_\beta(\boldsymbol{r}')\right)^* \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \left(\hat{R}^{\boldsymbol{\omega}} \phi_\chi(\boldsymbol{r})\right) \left(\hat{R}^{\boldsymbol{\omega}} \phi_\gamma(\boldsymbol{r}')\right) d^3r \, d^3r'$$

$$= \sum_{\alpha'\beta'\chi'\gamma'} \left(D^l_{\alpha',\alpha}(\boldsymbol{\omega})\right)^* \left(D^l_{\beta',\beta}(\boldsymbol{\omega})\right)^* V_{\alpha'\beta',\chi'\gamma'} D^l_{\chi',\chi}(\boldsymbol{\omega}) D^l_{\gamma',\gamma}(\boldsymbol{\omega})$$

V is a rotationally invariant fourth-rank tensor of angular momentum *l*

s-orbital case

There is only one non-zero Coulomb matrix element, $V_{\alpha\alpha,\alpha\alpha}$, which is called the Hubbard parameter and denoted U_0.

$$
\begin{aligned}
\hat{V} &= \frac{1}{2} U_0 \sum_{\zeta,\zeta'} \hat{c}^\dagger_{\alpha,\zeta} \hat{c}^\dagger_{\alpha,\zeta'} \hat{c}_{\alpha,\zeta'} \hat{c}_{\alpha,\zeta} \\
&= \frac{1}{2} U_0 \left(\hat{c}^\dagger_{\alpha,\uparrow} \hat{c}^\dagger_{\alpha,\downarrow} \hat{c}_{\alpha,\downarrow} \hat{c}_{\alpha,\uparrow} + \hat{c}^\dagger_{\alpha,\downarrow} \hat{c}^\dagger_{\alpha,\uparrow} \hat{c}_{\alpha,\uparrow} \hat{c}_{\alpha,\downarrow} \right) \\
&= U_0 \hat{n}_{\alpha,\uparrow} \hat{n}_{\alpha,\downarrow}
\end{aligned}
$$

p-orbital case

- The general form of an invariant fourth-rank Cartesian tensor is

$$V_{\alpha\beta,\chi\gamma} = U\delta_{\alpha\chi}\delta_{\beta\gamma} + J\delta_{\alpha\gamma}\delta_{\beta\chi} + J'\delta_{\alpha\beta}\delta_{\chi\gamma}$$

where $U = V_{\alpha\beta,\alpha\beta}$, $J = V_{\alpha\beta,\beta\alpha}$, and $J' = V_{\alpha\alpha,\beta\beta}$ (all with $\alpha \neq \beta$).

- Since the orbitals are real, $V_{\alpha\beta,\chi\gamma} = V_{\chi\beta,\alpha\gamma} = V_{\alpha\gamma,\chi\beta}$, implying $J = J'$.

- The $3^4 = 81$ interaction matrix elements can all be expressed in terms of 2 independent parameters.

$$V_{\alpha\beta,\chi\gamma} = U\delta_{\alpha\chi}\delta_{\beta\gamma} + J(\delta_{\alpha\gamma}\delta_{\beta\chi} + \delta_{\alpha\beta}\delta_{\chi\gamma})$$

The corresponding interaction operator is

$$\hat{V} = \frac{1}{2}\left[(U - J)\colon \hat{n}^2\colon -4J\colon \hat{S}^2\colon -J\colon \hat{L}^2\colon\right]$$

$$= \frac{1}{2}\left[(U - \frac{1}{2}J)\colon \hat{n}^2\colon -2J\colon \hat{S}^2\colon +J\sum_{\alpha\beta}\colon (\hat{n}_{\alpha\beta})^2\colon\right]$$

where $\hat{\boldsymbol{L}}$ is the orbital angular momentum, $\hat{\boldsymbol{S}}$ is the spin angular momentum, and

$$\colon (\hat{n}_{\alpha\beta})^2\colon = 2\left(\hat{c}_{\alpha,\uparrow}\hat{c}_{\alpha,\downarrow}\right)^{\dagger}\left(\hat{c}_{\beta,\uparrow}\hat{c}_{\beta,\downarrow}\right)$$

represents hopping of singlet pairs of electrons from one spatial orbital to another.

d-orbital case

The $5^4 = 625$ elements of the interaction matrix can all be written in terms of 3 independent parameters.

$$\hat{V} = \frac{1}{2}\left[(U - \frac{1}{2}J + 5\Delta J) : \hat{n}^2 : -2(J - 6\Delta J) : \hat{S}^2 : \right.$$
$$\left. + (J - 6\Delta J)\sum_{\alpha\beta} : (\hat{n}_{\alpha\beta})^2 : +\frac{2}{3}\Delta J : \hat{Q}^2 : \right]$$

Comparison with the Stoner Hamiltonian

- For *p* and *d* shells, the scalar and vector Stoner Hamiltonians are:

$$\hat{V}_{\text{Stoner}} = \frac{1}{2}(U - \frac{1}{2}J) \colon \hat{n}^2 \colon - J \colon \hat{S}_z^2 \colon$$

$$\hat{V}_{\text{Stoner}} = \frac{1}{2}(U - \frac{1}{2}J) \colon \hat{n}^2 \colon - J \colon \hat{S}^2 \colon$$
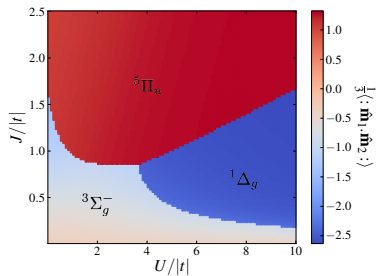
(The vector version is equivalent to the Hamiltonian of Dworin and Namath.)
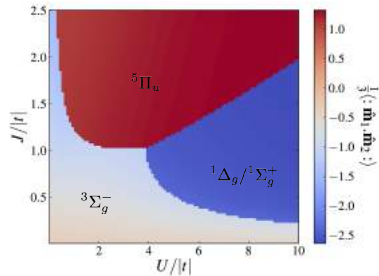
- The interaction matrix

$$V_{\alpha\beta,\chi\gamma} = U\delta_{\alpha\chi}\delta_{\beta\gamma} + J\delta_{\alpha\gamma}\delta_{\beta\chi}$$

looks like the general *p*-shell result but is missing the $J\delta_{\alpha\beta}\delta_{\chi\gamma}$ (pair-hopping) term. Consequently, it is not invariant on interchange of α with χ or β with γ.

p-dimer phase diagram

Full Hamiltonian

Stoner Hamiltonian

Conclusions

- Semi-empiricial TB is fun and easy. Try it!
- Ab initio self-consistent TB is not so bad, either.
- Check the form of any multi-band Hubbard model you may be using.