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INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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H4.SMR/994-11

SPRING COLLEGES IN COMPUTATIONAL PHYSICS

19 May - 27 June 1997

ELECTRONS IN SOLIDS - II

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THE TIGHT-BINDING TECHNIQUE

The basic idea behind the tight-binding technique is to search for a basis which is denumerable infinite, reasonably localized on atoms or groups of atoms which constitute the solid, and in which basis the representation of the hamiltonian is a sparse matrix.

The potential seen by an electron in a solid near one of its constituent atoms is not very different from the isolated atomic potential. However, the potential is rather different in the interstitial region. Here the solid potential is rather flat. One simple choice of the basis is the local atomic orbitals.

Let us expand the wave-function in this basis :

$$\Psi_{\underline{k}}(\underline{r}) \;=\; \sum_n c_n \, \phi(\underline{r} \,-\, \underline{r}_n)$$

The Bloch Theorem then implies that :

$$\Psi_{\underline{k}}(\underline{r}) \;=\; \sum_n \exp\left(\imath \underline{k}.\underline{r}_n\right) \phi(\underline{r} \,-\, \underline{r}_n)$$

If we now notice that the basis functions satisfy :

$$T\phi(\underline{r} - \underline{r}_n) + U(\underline{r} - \underline{r}_n)\phi(\underline{r} - \underline{r}_n) = E_0\,\phi(\underline{r} - \underline{r}_n) \qquad (1)$$

The Schrödinger equation gives :

$$T\Psi_{\underline{k}}(\underline{r}) + \sum_n V(\underline{r} - \underline{r}_n)\Psi_{\underline{k}}(\underline{r}) \qquad (2)$$

Gathering together equations (1) and (2) and using the Bloch representation : Also assuming that the basis is *orthogonal* which in fact a simple atomic basis is not.

$$(E - E_0)\Psi_{\underline{k}}(\underline{r}) = \sum_n \exp(i\underline{k}.\underline{r}_n)W(\underline{r} - \underline{r}_n)\phi(\underline{r} - \underline{r}_n)$$

Multiplying by $\Psi^*_{\underline{k}}(\underline{r})$ and integrating over all space :

$$E = E_0 + \sum_n \exp(i\underline{k}.\underline{r}_n)\int d^3\underline{r}\phi^*(\underline{r} - \underline{r}_n)W(\underline{r})\phi(\underline{r})$$

where : W($\underline{r}$) = V($\underline{r} - \underline{r}_n$)-U$\underline{r} - \underline{r}_n$)

EXAMPLE : A LINEAR CHAIN

Suppose :

$$\begin{aligned} \int_{-\infty}^{\infty} \phi^*(x)\, W(x)\, \phi(x) dx &= -\alpha \quad (\alpha > 0) \\ \int_{-\infty}^{\infty} o*(x-a)\, W(x)\, \phi(x) dx &= -\beta \quad (\beta > 0) \\ \int_{-\infty}^{\infty} o*(x+a)\, W(x)\, \phi(x) dx &= \beta' \end{aligned}$$

All other integrals are supposed to be small.

Case 1 : If the atomic orbitals are symmetric : $\beta' = -\beta < 0$

$$E_s = E_0 - \alpha_s - 2\beta_s \cos(ka)$$

Case 2 : If the atomic orbitals are antisymmetric $\beta' = -\beta > 0$

$$E_a = E_0 - \alpha_a + 2\beta_a \cos(ka)$$

BAND CROSSING AND HYBRIDIZATION

So far we have expanded the wavefunction only in terms of symmetric or antisymmetric atomic orbitals. Let us now extend the basis and include both types :

$$
\begin{aligned}
\Psi_{\underline{k}}(\underline{r}) &= A_1\Psi^s_{\underline{k}}(\underline{r}) + A_2\Psi^a_{\underline{k}}(\underline{r}) \\
\Psi^s_{\underline{k}}(\underline{r}) &= \sum_n \exp(\imath\underline{k}.\underline{r}_n)\phi_s(\underline{r} - \underline{r}_n) \\
\Psi^a_{\underline{k}}(\underline{r}) &= \sum_n \exp(\imath\underline{k}.\underline{r}_n)\phi_a(\underline{r} - \underline{r}_n)
\end{aligned}
$$

Putting this into the Schrödinger equation and using orthogonality we get :

$$
\begin{aligned}
A_1(E - E_s) + A_2E_{12} &= 0 \\
A_1E_{21} + A_2(E - E_a) &= 0
\end{aligned}
$$

where

$$
\begin{aligned}
E_{12} &= \sum_n \exp(\imath\underline{k}.\underline{r}) \int d^3\underline{r}\phi *_s (\underline{r} - \underline{r}_n)W(\underline{r})\phi_a(\underline{r}) \\
E_{21} &= \sum_n \exp(\imath\underline{k}.\underline{r}) \int d^3\underline{r}\phi *_a (\underline{r} - \underline{r}_n)W(\underline{r})\phi_s(\underline{r})
\end{aligned}
$$

Four our linear chain example we have :

n=0 term in the sum vanishes because of the antisymmetry of the integrand. The leading terms are :

n=1 : $E_{12} = 2\gamma \sin(ka)$
n=1 : $E_{21} = 2\gamma' \sin ka$

The set of equations have a solution if :

$$(E - E_s(k))(E - E_a(k)) \; - \; +4\gamma\gamma' \sin^2(ka) \; = \; 0$$

This has two solutions :

$$E^+ = \frac{1}{2}\left[(E_a + E_s) + \sqrt{(E_a - E_s)^2 + 4\gamma\gamma' \sin^2(ka)}\right]$$
$$E^- = \frac{1}{2}\left[(E_a + E_s) - \sqrt{(E_a - E_s)^2 + 4\gamma\gamma' \sin^2(ka)}\right]$$

Suppose the bands don't cross : then

at k=0 : $E^+ = E_0 - \alpha_a + 2\beta_a$ and
$E^- = E_0 - \alpha_s - 2\beta_s$

at k= π/a: $E^+ = E_0 - \alpha_a - 2\beta_a$ and
$E^- = E_0 - \alpha_s + 2\beta_s$

and $-\alpha_a - 2\beta_a > -\alpha_s + 2\beta_s$

Suppose the branches cross and at k=k_1, $E_s(k_1) = E_a(k_1) = E_c$

At k=k_1 :

$$E^+ = E_c + \sqrt{\gamma\gamma'}\sin(k_1 a)$$
$$E^- = E_c - \sqrt{\gamma\gamma'}\sin(k_1 a)$$

The + branch always remains above the E_c and the - branch always below. The limits at the Brillouin Zone boundary are :

at k= π/a: $E^- = E_0 - \alpha_a - 2\beta_a$ and
$E^+ = E_0 - \alpha_s + 2\beta_s$

Hybridization tends to open a gap at the band crossing. Again ,

At k=0.
for the - branch : A_1=0, A_2=1 → symmetric
for the + branch : A_1=1, A_2=0 → anti-symmetric

At k=π/a.
for the + branch : A_1=0, A_2=1 → symmetric
for the - branch : A_1=1, A_2=0 → anti-symmetric

In between the coefficients are neither 0 nor 1, so there is mixed symmetry.

Hybridization tends to make angular momentum labeling no longer suitable.

3-D CRYSTAL LATTICES

The generalization is straightforward. For example if we only retain the diagonal element -I and the nearest-neighbour off diagonal elements -J. then

for the b.c.c. lattice :

$$E = E_0 - I - 8J \cos(k_x a/2)\cos(k_y a/2)\cos(k_z q/2)$$

for the f.c.c. lattice :

$$E = E_0 - I - 4J\,(\cos(k_y a/2)\cos(k_z a/2) + \cos(k_z a/2) \cos(k_x a/2) + \cos(k_x a/2)\cos(k_y a/2))$$

SILICON

Silicon (or Germanium) crystallizes inn the diamond lattice. Each atom has four nearest neighbours. The outermost electrons of Si are s^2p^2 in the atom. Since these two levels are almost degenerate. in the solid they hybridized and form the four sp^3 hybridized orbitals which bond with the four nearest neighbours in a tetrahedral covalent bonding configuration.

The diamond lattice can be thought of as a fcc lattice with two atoms per unit cell : one at (000) and the other (1/4,1/4,1/4)d along the diagonal ($d=\sqrt{3}a$). The unit cell of the f.c.c. lattice is shown in the figure.

Thus in there are eight orbitals per unit cell.

Basis : $\phi_{m,\alpha,n}(r)$ where m goes over the four sp^3 hybridized orbitals on the atom labeled by α in the n-th unit cell.

$$\begin{aligned} \phi_{m,1,n} &= \phi_m(\underline{r} - \underline{r}_n) \\ \phi_{m,2,n} &= \phi_m(\underline{r} - \underline{r}_n - \underline{b}) \end{aligned}$$

where : $\underline{b} = (1/4,1/4,1/4)d$.

The secular equation involves a 8×8 determinant :

$$||E\mathbf{I} - \mathbf{H}_0 - \mathbf{H}_1 S(\underline{k})|| = 0$$

$$(\cos(k_y a/2)\cos(k_z a/2) + \cos(k_z a/2)\cos(k_x a/2) + \cos(k_x a/2)\cos(k_y a/2)) \;=\; S(\underline{k})$$

The eight solutions of the above secular determinant gives the eight valence and the eight conduction bands.

DIFFICULTIES

The LCAO tight-binding described above has several difficulties :

1. The basis is not really orthogonal. The secular determinant involves an overlap matrix **S** rather than **I**. This problem can be overcome by orthogonalizing the basis set. This immediately leads to the problem than the off-diagonal matrices (which were earlier almost nearest neighbour) become long ranged. sparseness is lost and this immediately detracts from the advantage of a tight-binding formulation.
2. The basis is restricted to only the lower valence states. This gives a good description of the wavefunction near the atoms. but is not good in the interstitial. Inclusion of higher valence states increases the rank of the secular determinant and makes computational that much more difficult. Unbound continuum cannot be taken into account at all.
3. The basis is overcoomplete and there may be linear dependences. This would mean that the overlap matrix has a zero eigenvalue and the secular determinant is trivially satisfied for all values of E. Even

if the eigenvalue is small, the actual computation of the low lying E's become inaccurate.

if the eigenvalue is small, the actual computation has a corresponding loss of accuracy in E.

Long experience of chemists show that many of the properties of solids and molecules are dominated by short-range interactions : the local chemistry of the system. The equilibrium distance in a covalent bond varies little from one crystal to another. So do many properties like force constants, dipole moments and polarizabilities. This **transferability** , for example, allows us to deduce about the local structure in an amorphous semiconductor to be deduced from its infra-red and Raman vibration spectra.

MODERN QUANTITATIVE FORMS OF TIGHT-BINDING

WANNIER FUNCTIONS

Let us consider the wave-function corresponding to a particular band (labeled by b) :

$$H\Psi_{\underline{k},b}(\underline{r}) \;=\; E_{\underline{k},b}\Psi_{\underline{k},b}(\underline{r})$$

These functions obey the Bloch Theorem and are orthonormal for different values of $\underline{k}$.

$$\int_{u.c.} d^3\underline{r}\ \Psi^*_{\underline{k}}(\underline{r})\Psi_{\underline{k}'}(\underline{r}) \ = \ \delta(\underline{k} \ - \ -\underline{k}')$$

The Wannier functions are defined by :

$$W_b(\underline{r} - \underline{r}_n) \ = \ N^{-1/2}\sum_{\underline{k}} \exp\left(-\imath\underline{k}.\underline{r}_n\right)\Psi_{\underline{k},b}(\underline{r})$$

These functions are also orthonormal :

$$\langle W_b(\underline{r} - \underline{r}_n)|W_{b'}(\underline{r} - \underline{r}_m)\rangle \ = \ \delta_{bb'}\delta_{nm}$$

Inversion yields :

$$\Psi_{\underline{k},b}(\underline{r}) \ = \ N^{-1/2}\sum_{n} \exp\left(\imath\underline{k}.\underline{r}_n\right)W_b(\underline{r} \ - \ \underline{r}_n)$$

The choice of the phase is so taken that the phase of W(0) is real and positive. This results in the Wannier function having its maximum at the location $\underline{r}_n$ and decaying away from the lattice sites. The orthogonality requires the Wannier functions to have long oscillating tails. Thus localization is not really achieved.

Construction of Wannier functions are carried out by a variational procedure. First of all trial wave functions are chosen with the correct symmetry, but no orthogonality : $F_b(\underline{r} \ - \ \underline{r}_n;\{\alpha_s\})$. Out of these an orthogonal

set is prepared again with the correct symmetry. (This is done to avoid the orthogonalization catastrophe). The parameters are determined by the variational minimization of the functional :

$$\epsilon \;=\; \sum_b \frac{\langle W_b(\underline{r})|H|W_b(\underline{r})\rangle}{\langle W_b(\underline{r})|W_b(\underline{r})\rangle}$$

See Kohn and Onffroy , Phys. Rev. B10, 448 (1973)

Once the Wannier functions are set up, we use these as the tight-binding basis set as before. The secular equation follows :

$$||E\mathbf{I} - H_{bb'}(\underline{k})|| \;=\; 0$$

where : i

$$H_{bb'}(\underline{k}) \;=\; \sum_n \exp\left(i\underline{k}.\underline{r}_n\right) \int W_b^*(\underline{r}) H W_{b'}(\underline{r} \;-\; \underline{r}_n)$$

Again, the basis is useful only if the overlaps are short-ranged.

THE CHEMICAL PSEUDO-POTENTIAL

Localized orbitals theory works if the distortions associated with neighbouring environments are small and the orbitals associated with the

atoms or groups of them can be used as a basis of building up the solid out of the "building blocks". The building blocks are **chemically invariant** and need not be recalculated for every new system. This is the idea of **transferability**. Wannier functions have long orthogonality based tails which sample distant environment, and are therefore not really tight-binding. Can we set up such localized basis set ?

See : Anderson P.W., Phys Rev Lett 21, 13 (1968) : Phys. Rev. 181,25 (1969) Weeks et.al. J. Chem. Phys. 58, 1388 (1973)

The first condition is that the localized functions must belong to the band subspace of the solid. If these are basis for expansion of wave functions in the band, then they should belong to the same subspace and not be outside it.

Define the projection operator on the band as :

$$\mathcal{P} = \sum_{\underline{k}} |\Psi_{\underline{k}}\rangle\langle\Psi_{\underline{k}}|$$

and :

$$|\phi_n\rangle = \mathcal{P}|\phi_n\rangle$$

This leads to :

$$H|\phi_n\rangle \; - \; \mathcal{P}H\mathcal{P}|\phi_n\rangle \; = \; 0 \qquad (3)$$

Let H_n correspond to the isolated atom/molecular building block and

$$H_n|\phi_n^0\rangle \; = \; E_n^0|\phi_n^0\rangle$$

The localized orbitals we want differ from these isolated atom orbitals. If the effect of the environment is small, then they differ but little and the localized orbitals we want are distortions of the atomic orbitals - distorted by the bonding with the environment.

The basis is built up by trying to satisfy the above equation with the *distorted* form orbitals ϕ_n as closely as we can in the given subspace.

$$\mathcal{P}H_n\mathcal{P}|\phi_n\rangle \; = \; E_n|\phi_n\rangle \qquad (4)$$

If we add up the above two numbered equations we obtain :

$$\{H_n \; + \; (U_n \; - \; \mathcal{P}U_n\mathcal{P})\}\,|\phi_n\rangle \; = \; E_n|\phi_n\rangle \qquad (5)$$

where,

$$U_n \;=\; H \;-\; H_n \;=\; \sum_{m \neq n} V_m^n$$

where V_m^n is the perturbation induced by the atom m on the potential at the atom n.

Moreover, the new basis so derived (from each atom) pans the entire band subspace :

$$\mathcal{P} \;=\; \sum_n \sum_m |\phi_n\rangle S_{nm}^{-1} \langle \phi_m|$$

Andersen argued that the rather complicated projection operator above can be replaced by the much simpler $\mathcal{P}_m$ on the neighbouring atoms. This reduced the defining equation in a much simpler form :

$$H|\phi_n\rangle \;=\; E_n|\phi_n\rangle \;+\; \sum_m |\phi_m\rangle\langle\phi_m|V_m^n|\phi_n\rangle$$

We shall now use this basis and expand the wavefunction in the band as a linear combination. The usual variational principle then yields the secular equation :

$$||E\delta_{nm} \;-\; D_{nm}|| \;=\; 0$$

where,

$$D_{nn} = E_n = E_n^0 + \sum\{\langle|\phi_n^0|V_m^n|\phi_n^0\rangle - \langle\phi_n^0|\phi_m^0\rangle\langle\phi_m^0|V_m^n|\phi_n^0\rangle\}$$

and

$$D_{nm} = \langle\phi_n|V_{nn}^n|\phi_m\rangle$$

Note that since, unless we have all atoms exactly alike, $V_{nn}^n \neq V_n^{nn}$, So, in general, pseudo-hamiltonian D is not symmetric.We have reduced the situation to one in which the secular equation resembles that of a orthonormal basis, but the pseudo-hamiltonian is not symmetric. In fact, $D = S^{-1} H$.