

EQUIVALENCE BETWEEN THE OVERLAP REDUCED SEMIEMPIRICAL TIGHT BINDING AND THE
CHEMICAL PSEUDOPOTENTIAL METHODS IN BAND STRUCTURE CALCULATIONS:
A NEW SIMPLE APPROACH TO WAVE-FUNCTION LOCALIZATION IN CRYSTALS

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The semiempirical approximations to the tight binding electronic band structure in crystals are discussed, and it is shown that a procedure exists (ORSTB), by which the secular equation matrix elements are made to coincide with those of the chemical pseudopotential method. This gives a formal theoretical basis to many of the practical prescriptions used until now in successful tight binding calculations. The case of selenium is considered to exemplify the ORSTB procedure.

I. The Semiempirical Tight Binding: Approaches and Procedures

The tight binding (TB) method has often provided in the past a useful semiempirical scheme to compute the electronic band structure of several materials (see, e.g., [1] and [2]). The semiempirical TB (STB) introduces three main approximations: i) all the three-centre integrals are neglected, ii) The crystal field is neglected, or, if retained, it is strongly reduced with respect to the computed one. iii) Both overlap and interaction two-centre integrals are slightly decreased with respect to the computed ones. The corrective parameters introduced for the approximation iii), or for both iii) and ii), are determined in such a way that the bands reproduce some experimental features of the material.

While the approximation i) above has an essentially practical origin, and it rests on the relative smallness of three- with respect to two-centre integrals, no physical interpretation has yet been proposed for ii), which still stands only as a practical prescription. The reason for iii), on the contrary, has been sought in the fact the TB Bloch sums should not be made with free-atom eigenfunctions, but rather with atomic-like functions contracted in the direction of the bonds to account for the crystal environment [1]. This amounts to saying that screened (localized) orbitals [3] must be used to improve the TB accuracy, and that iii) introduces in some way the correction required when free-atom orbitals are used in place of the localized ones. This hint suggests the way to comprehend all the STB approximations in a unique formulation.

First of all, we consider Bloch sums made with the localized orbitals as they are obtained in the framework of the chemical pseudopotential (CP) approach [4,5]. The non-hermitian localizing CP hamiltonian (LCPH) can be re-defined, with respect to the original formulation, so that also open shell atomic constituents can be taken into account, as it is usual in TB. Moreover, with the LCPH introduced here, the crystal bands are obtained by solving a secular equation for a hermitian operator. Its matrix elements - this is the key point of our argument - become equivalent to those obtained in the STB when free-atom orbitals are used, provided that the requirements i) and ii) above are still met, and iii) is substituted by the following: iii') overlap integrals *only* must be strongly reduced in magnitude, whilst interaction integrals are retained as they are computed.

The set of prescriptions i), ii) and iii') characterizes the overlap reduced

STB (ORSTB) method. This procedure achieves three main results. First, the relationship between localization of atomic-like orbitals and STB is clearly stated, and a short way is suggested to account for localization effects still using free-atom orbitals. Then, while the standard STB approximations were unrelated and only of practical origin, ORSTB shows that they, once exactly stated, have a common theoretical origin, and cannot be used separately. Finally, the reason is understood why STB was so fairly successful, in spite of its quite rough approximations. Conversely, where STB fails (as in reproducing the correct width of some bands), ORSTB gives results in excellent agreement with other more sophisticated methods and with experiments (see, e.g., the case of GaSe-type crystals [6]).

II. The Chemical Pseudopotential Revisited

In the crystal we consider, $\vec{n}$ indicates a generic lattice vector, and $\vec{s}$, $\vec{s}'$ or $\vec{s}''$ are the basis sites in the fundamental cell. The standard CP procedure [4,5] considers, for each centre $\vec{s}$, both the free hamiltonian $H^0(\vec{s})$ and the LCPH, $H^P(\vec{s})$, of the atom (or ion) centred at $\vec{s}$. Their eigenvalues and eigenvectors are identified by appropriate sets of quantum numbers, indicated by ℓ^0 and ℓ :

$$H^0(\vec{s})|\ell^0, \vec{s}\rangle = \epsilon^0(\ell^0, \vec{s})|\ell^0, \vec{s}\rangle, \quad (1)$$

$$H^P(\vec{s})|\ell, \vec{s}\rangle = \epsilon(\ell, \vec{s})|\ell, \vec{s}\rangle. \quad (2)$$

Of course, for $\vec{n}$ whatever, $H^P(\vec{s}+\vec{n})$ has the same eigenvalues as $H^P(\vec{s})$, and also $|\ell, \vec{s}\rangle$ and $|\ell, \vec{s}+\vec{n}\rangle$ differ only in their being centred in different cells. The one-electron crystal potential is usually the sum of short ranged separate contributions of each centre of the lattice [5,7]. By picking out the free hamiltonian of a centre ($\vec{s}$, for instance), the crystal one-electron hamiltonian becomes

$$H = H^0(\vec{s}) + \sum_{\vec{s}', \vec{n}} V(\vec{s}'+\vec{n}). \quad (3)$$

In eq.(3), and in the following, Σ' indicates that $\vec{n}=0$ is dropped if $\vec{s}=\vec{s}'$ or $\vec{s}=\vec{s}''$.

We define the LCPH for the centre $\vec{s}$ as follows

$$H^P(\vec{s}) = H^0(\vec{s}) + \sum_{\vec{s}', \vec{n}} \{V(\vec{s}'+\vec{n}) - P(\vec{s}'+\vec{n}) \frac{1}{2} [V(\vec{s}'+\vec{n}) + V(\vec{s})]\}, \quad (4)$$

$$P(\vec{s}'+\vec{n}) = \sum_{\ell} |\ell, \vec{s}'+\vec{n}\rangle \langle \ell, \vec{s}'+\vec{n}|. \quad (5)$$

Due to the screening effect of $P(\vec{s}'+\vec{n})$ in eq.(4), $H^P(\vec{s})$ and $H^0(\vec{s})$ do not differ too much, and each $|\ell, \vec{s}\rangle$ may be obtained by perturbation from a given $|\ell^0, \vec{s}\rangle$. When the free atom (ion) at $\vec{s}$ is open shell, both occupied and unoccupied eigenstates of $H^0(\vec{s})$ are degenerate by spherical symmetry, and this degenerate manifold corresponds to a set of states (the degeneracy is often removed) $|\ell, \vec{s}\rangle$, all of which we include in our theory, and, for the appropriate $\vec{s}'$, in the operators of eq.(5).

From each one of the $|\ell, \vec{s}\rangle$ taken into account above, and for a given $\vec{k}$ in the Brillouin zone, a Bloch sum $|\vec{k}, \ell, \vec{s}\rangle$ is obtained. It is easily verified from eqs. (2), (3), (4), and (5) that

$$H|\vec{k}, \ell, \vec{s}\rangle = \sum_{\ell', \vec{s}'} D(\vec{k})_{\ell, \vec{s}; \ell', \vec{s}'} |\vec{k}, \ell', \vec{s}'\rangle, \quad (6)$$

$$D(\vec{k})_{\ell, \vec{s}; \ell', \vec{s}'} = \epsilon(\ell, \vec{s}) \delta_{\ell\ell'} \delta_{\vec{s}\vec{s}'} + \sum_{\vec{n}} \exp(i\vec{k} \cdot \vec{n}) \langle \ell', \vec{s}' | \frac{1}{2} [V(\vec{s}') + V(\vec{s}+\vec{n})] | \ell, \vec{s}+\vec{n} \rangle. \quad (7)$$

Finally, electronic eigenstates and energies for the crystal are obtained by solving the secular equation for the matrix D of eq.(7)

$$\det[D(\vec{k}) - EI] = 0. \quad (8)$$

In eq.(4), $\frac{1}{2} [V(\vec{s}'+\vec{n}) + V(\vec{s})]$ replaces the simple $V(\vec{s}'+\vec{n})$ of the standard CP. Due to this, our matrix D , eq.(7), is hermitian, even if the LCPH of eq.(4) is not. Moreover, in the standard CP, the sum in eq.(5) is restricted to the occupied orbitals only. Were this requirement satisfied, eq.(4) would still define an Adams-Gilbert hamiltonian [5]. If, however, in eq.(5) $P(\vec{s}'+\vec{n})$ defines a manifold inclusive also of empty states, the screening due to P admittedly increases, and $|\ell, \vec{s}\rangle$ tends to $|\ell^0, \vec{s}\rangle$ (they coincide in the limit a complete set of functions, when $P=1$), but conversely also the dimension of the secular equation (8) increases,

and the accuracy of the crystal eigenfunctions is, at least in part, recovered.

III. The Overlap Reduced Semiempirical Tight Binding

In the standard TB, the Bloch sum are made with the free orbitals of eq.(1). As usual [6], the matrix elements of H are obtained by picking out in eq.(3) first $H^0(\vec{s})$ and then $H^0(\vec{s}'+\vec{n})$, by averaging the two results (hermiticity is thus preserved, in spite of any approximation), and by neglecting three-centre integrals:

$$H^{av}(\vec{k})_{\ell^0\vec{s},\ell^0\vec{s}'} = \frac{1}{2}[\epsilon^0(\ell^0,\vec{s}) + \epsilon^0(\ell^0,\vec{s}')]S(\vec{k})_{\ell^0\vec{s},\ell^0\vec{s}'} + K_{\ell^0\vec{s},\ell^0\vec{s}'} + V^{av}(\vec{k})_{\ell^0\vec{s},\ell^0\vec{s}'} \quad (9)$$

$$S(\vec{k})_{\ell^0\vec{s},\ell^0\vec{s}'} = \sum_{\vec{n}} \exp(i\vec{k}\cdot\vec{n}) \langle \ell^0, \vec{s} | \ell^0, \vec{s}'+\vec{n} \rangle \quad (10)$$

$$K_{\ell^0\vec{s},\ell^0\vec{s}'} = \delta_{\vec{s}\vec{s}'} \sum_{\vec{n}} \langle \ell^0, \vec{s} | V(\vec{s}'+\vec{n}) | \ell^0, \vec{s} \rangle \quad (11)$$

$$V^{av}(\vec{k})_{\ell^0\vec{s},\ell^0\vec{s}'} = \sum_{\vec{n}} \exp(i\vec{k}\cdot\vec{n}) \langle \ell^0, \vec{s} | \frac{1}{2}[V(\vec{s})+V(\vec{s}'+\vec{n})] | \ell^0, \vec{s}'+\vec{n} \rangle \quad (12)$$

Equation (12) already contains i) of ORSTB. The crystal eigenvalues are obtained by solving the secular equation $\det|H^{av}(\vec{k})-ES(\vec{k})|=0$, or equivalently

$$\det|S(\vec{k})^{-\frac{1}{2}}H^{av}(\vec{k})S(\vec{k})^{-\frac{1}{2}}-E\mathbf{I}|=0 \quad (13)$$

We introduce now in eq.(13) the other ORSTB prescriptions. As far as ii) is concerned, we first define the screened crystal field K^{sc} as

$$K_{\ell^0\vec{s},\ell^0\vec{s}'}^{sc} = K_{\ell^0\vec{s},\ell^0\vec{s}'} - \delta_{\vec{s}\vec{s}'} \sum_{\vec{n}} \langle \ell^0, \vec{s} | P(\vec{s}'+\vec{n}) \frac{1}{2}[V(\vec{s}'+\vec{n})+V(\vec{s})] | \ell^0, \vec{s} \rangle \quad (14)$$

where K , eq.(11), is the TB crystal field. Due to the screening effect of the term with P in eq.(14), K^{sc} is small, while K may not. Therefore, to apply ii), we substitute K^{sc} for K in eq.(9) and thus in eq.(13). We see that K^{sc} gives also the difference between free and localized eigenvalues. In fact, from eq.(4),

$$\langle \ell^0, \vec{s} | HP(\vec{s}) | \ell^0, \vec{s} \rangle = \epsilon^0(\ell^0, \vec{s})\delta_{\ell^0\ell^0} + K_{\ell^0\vec{s},\ell^0\vec{s}}^{sc} \quad (15)$$

which, for $\ell^0=\ell^0$ gives $\epsilon(\ell, \vec{s})$ in the first order perturbation theory. By taking into account also the off-diagonal elements in eq.(15), and by diagonalizing, we get a variational estimate of $\epsilon(\ell, \vec{s})$. By the way, it is worth noting that three-centre integrals should be taken into account only if functions not centred at $\vec{s}$ were considered in the variational computation of $\epsilon(\ell, \vec{s})$. Also i), therefore, is accounted for by the choice of K^{sc} replacing the TB crystal field.

The prescription iii') of ORSTB requires that $\alpha \langle \ell^0, \vec{s} | \ell^0, \vec{s}'+\vec{n} \rangle$ is substituted for the overlap integral $\langle \ell^0, \vec{s} | \ell^0, \vec{s}'+\vec{n} \rangle$. In principle, α is $\vec{k}$ -, orbital- and site-dependent, but in the practice only one, or at most a few different values are used, with the only requisite that $|\alpha| \ll 1$. Therefore, the overlap matrix, eq.(10), reads as $S(\alpha, \vec{k}) = \mathbf{I} + \Delta(\alpha, \vec{k})$, where $\Delta(\alpha, \vec{k})$ is a small correction to $\mathbf{I}$ of the same order as α . Since $S(\alpha, \vec{k})$ appears also in eq.(9), $H^{av}(\vec{k})$ as well becomes $H^{av}(\alpha, \vec{k})$, and accordingly the TB secular equation (13) is changed into

$$\det|S(\alpha, \vec{k})^{-\frac{1}{2}}H^{av}(\alpha, \vec{k})S(\alpha, \vec{k})^{-\frac{1}{2}}-E\mathbf{I}|=0 \quad (16)$$

By using the Löwdin expansion for $S(\alpha, \vec{k})^{-\frac{1}{2}}$, we get to the first order in α

$$S(\alpha, \vec{k})^{-\frac{1}{2}}H^{av}(\alpha, \vec{k})S(\alpha, \vec{k})^{-\frac{1}{2}} = H^{av}(\alpha, \vec{k}) - \frac{1}{2}[\Delta(\alpha, \vec{k})H^{av}(0, \vec{k}) + H^{av}(0, \vec{k})\Delta(\alpha, \vec{k})] \quad (17)$$

For each site, we define the difference between localized and free orbitals, $|\delta\ell, \vec{s}\rangle = |\ell, \vec{s}\rangle - |\ell^0, \vec{s}\rangle$, and we substitute accordingly $|\ell, \vec{s}\rangle \rightarrow |\delta\ell, \vec{s}\rangle$ for the free orbitals in eq.(17). All the terms of eq.(17) where either $|\delta\ell, \vec{s}\rangle$ or K^{sc} appears may be considered of the same order in α as those where $\Delta(\alpha, \vec{k})$ appears. Therefore, retaining only the terms of the first order in α , eq.(17) becomes

$$S(\alpha, \vec{k})^{-\frac{1}{2}}H^{av}(\alpha, \vec{k})S(\alpha, \vec{k})^{-\frac{1}{2}} = \mathbf{E}^0 + K^{sc} + U^{av}(\vec{k}) - Q(\alpha, \vec{k}) \quad (18)$$

$$Q(\alpha, \vec{k}) = \delta V(\vec{k}) + \frac{1}{2}[\Delta(\alpha, \vec{k})V^{av}(\vec{k}) + V^{av}(\vec{k})\Delta(\alpha, \vec{k})] \quad (19)$$

$$\mathbf{E}_{\ell^0\vec{s},\ell^0\vec{s}'}^0 = \delta_{\ell^0\ell^0}\delta_{\vec{s}\vec{s}'}\epsilon^0(\ell^0, \vec{s}) \quad (20)$$

$$\delta V(\vec{k})_{\ell^{\circ}, \vec{s}, \ell^{\circ}, \vec{s}'} = \sum_{\vec{n}} \exp(i\vec{k} \cdot \vec{n}) \{ \langle \ell^{\circ}, \vec{s} | \frac{1}{2} [V(\vec{s}) + V(\vec{s} + \vec{n})] | \ell^{\circ}, \vec{s} + \vec{n} \rangle + \langle \ell^{\circ}, \vec{s} | \frac{1}{2} [V(\vec{s}) + V(\vec{s} + \vec{n})] | \ell^{\circ}, \vec{s}' + \vec{n} \rangle \} \quad (21)$$

The matrix $U^{av}(\vec{k})$ in eq.(18) is obtained from $V^{av}(\vec{k})$ of eq.(12) by substituting everywhere $|\ell, \vec{s}\rangle$ and $|\ell', \vec{s}'\rangle$ for $|\ell^{\circ}, \vec{s}\rangle$ and $|\ell^{\circ}, \vec{s}'\rangle$, respectively.

Finally, we recall the discussion concerning eq.(15), and we compare eq.(18) with eq.(7). It follows that the secular equations (8) and (16) coincide, provided that α is chosen in such a way that $Q(\alpha, \vec{k})$, eq.(19), vanishes. Therefore, the condition $Q(\alpha, \vec{k})=0$ represents the exact statement of iii'). The equivalence between ORSTB and CP is thus complete.

IV. ORSTB Electronic Energy Bands of Selenium

As an example, we have computed the energy bands of selenium with the ORSTB procedure, using eigenvalues [8] and very simple orbitals [9] of the free atom. The crystal potential (see [6]) is consistent with the atomic orbitals used. It is not in the spirit of the method to worry about the exact fulfilment of ii) and iii') in the form they have been stated in section III. We have simply introduced both one and two parameters, which have been determined so that the bands match the fundamental optical gap of about 2 eV. In the former case, Fig.(1a), we have used $\alpha=-0.38$ and the screened crystal field computed according to eq.(14). In the latter case, Fig.(1b), we still have only one factor, $\alpha=0.2$, multiplying the overlap integrals, but now the unscreened crystal field, eq.(11), has been computed and then

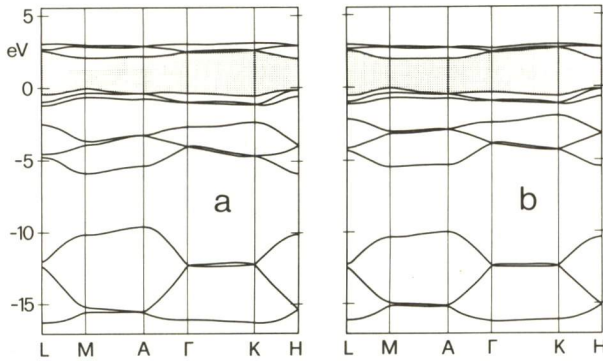


Fig.1. Bands of selenium with the ORSTB method
a) Screened crystal field, $\alpha=-0.38$. b) TB crystal field multiplied by $\beta=0.5$, $\alpha=0.2$: To agree with the current use for selenium bands, L and M label points on the $k_z=0$ and $k_z=\pi/2$ planes of the Brillouin zone, respectively

multiplied by $\beta=0.5$. The agreement with other calculations and with experiments is excellent (see, e.g., [10] as a recent comprehensive reference).

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