RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Self-consistent theory of overlap interactions in the tight-binding method

J. Dorantes-Dávila
Instituto de Física "Manuel Sandoval Vallarta," Universidad de San Luis Potosí, 78000 San Luis Potosí, Mexico

A. Vega
Departamento de Física Teórica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain

G. M. Pastor
Institut für Theoretische Physik der Universität zu Köln, Zülpicher Straße 77, W-5000 Köln 41, Germany

(Received 26 February 1993)

A local approach to overlap interactions in the tight-binding (TB) method is presented. The effects of overlap and local atomic environment on the orthogonalized interaction parameters are determined from a set of coupled linear equations. The accuracy of the method is demonstrated by calculations on transition metals and semiconductors having periodic and complex structures. This theory combines efficiently the simplicity of the orthogonal TB method with the transferability of the nonorthogonal approach, and is thus particularly useful for the study of complex systems.

Complex nonperiodic systems and low-dimensional systems (e.g., defects, surfaces, multilayers, thin films, and clusters) constitute, already for many years, one of the most active fields in condensed-matter physics. The importance of this subject for fundamental research and technological applications has motivated the work of numerous groups. Though remarkable progress has been achieved in a wide variety of problems, the determination of the electronic and structural properties of these materials remains a theoretical challenge. The lack of symmetry limits seriously the applications of conventional first-principles methods, such as the local-density approximation to density-functional theory, even if advantage is taken of the most recent developments in simulated annealing techniques.[1] In many cases of interest, the computational costs involved in such *ab initio* studies are so large that they become prohibitive. The development of simpler yet reliable approximate methods of calculation is therefore central to the progress in this field.

An alternative approach which has already provided numerous significant results is the realistic tight-binding (TB) method and related many-body models.[2–7] Here, a minimal basis set of localized atomiclike orbitals is considered for the valence electrons and the interactions are parametrized. Comparatively modest computing resources are required, while the quantum-mechanical essence of directional bonding and electronic correlations is preserved. A main concern, when applying the TB method to complex systems, has been the transferability of the interaction parameters from the local atomic environment where they were calculated or fitted (e.g., bulk crystal) to the environment of the specific problem under study (e.g., defect, surface, or cluster). As pointed out by several authors, this difficulty can be best overcome by using nonorthogonal and thus more localized basis orbitals.[7–12] However, working in an orthogonal basis remains appealing, since its simpler algebra has multiple advantages in both single-particle and many-body theories.[2] Therefore, and since the orthogonalization itself depends sensitively on the local environment of the atoms, efficient procedures for dealing with nonorthogonal basis in complex nonperiodic systems are sought.[7–12]

In this paper we first describe a simple method of determining *locally* the environment specific single-particle and two-particle interaction parameters corresponding to an orthogonal basis in terms of the interaction parameters and overlaps between nonorthogonal basis states. The accuracy and applicability of the theory are then demonstrated by calculations of the electronic spectrum of representative transition-metal and semiconductor systems having periodic and complex structures.

The starting point of our considerations is the known relation between the single-particle Hamiltonian matrix elements T_{ij} in Löwdin's orthonormal basis and the matrix elements $\tilde{T}_{ij}$ in the underlying nonorthogonal basis of atomiclike orbitals having overlaps S_{ij} ($S_{ii}=0$):[13]

$$T_{ij} = \sum_{l,m} [(1+S)^{-1/2}]_{il}\, \tilde{T}_{lm}\, [(1+S)^{-1/2}]_{mj} \; . \tag{1}$$

The indices i, j, etc. refer to both lattice site and atomic orbital α (e.g., $\alpha \equiv s,p,d$), and the sum runs over all basis orbitals. $T_{ii}=\varepsilon_i$ ($\tilde{T}_{ii}=\tilde{\varepsilon}_i$) stand thus for the energy levels and T_{ij} ($\tilde{T}_{ij}$) with $i \neq j$ for the hopping integrals in the orthogonal (nonorthogonal) basis. In order to introduce the self-consistent local approach we formally expand $(1+S)^{-1/2}$ in Taylor series around unity and rewrite Eq. (1) as

$$\begin{aligned} T_{ij} = \tilde{T}_{ij} &- \tfrac{1}{2}\sum_{l} (\tilde{T}_{il}S_{lj} + S_{il}\tilde{T}_{lj}) \\ &+ \tfrac{3}{8}\sum_{lk} (\tfrac{2}{3}S_{il}\tilde{T}_{lk}S_{kj} + \tilde{T}_{il}S_{lk}S_{kj} + S_{il}S_{lk}\tilde{T}_{kj}) \\ &+ O(S^3) \; . \end{aligned} \tag{2}$$

The above-mentioned environment dependence of T_{ij} can be clearly seen as resulting from the path summations, which involve the orbitals l, k, etc. at atoms surrounding the orbitals i and j. The nth-order correction to T_{ij} can be interpreted from a local point of view as the sum over all paths connecting i and j with one "interaction line" $\tilde{T}$ and n "overlap lines" S. This is illustrated in Fig. 1(a) by means of real-space diagrams for the terms up to first order in S. Unfortunately, retaining only the lowest-order terms in Eq. (2) is inadequate for realistic applications, particularly when sp electrons are involved. To include infinite orders in S we proceed in analogy to diagrammatic perturbation theory and replace the nonorthogonal ("undressed") interaction lines by orthogonal ("dressed") interaction lines in the first-order diagrams [see Fig. 1(b)]. The resulting first-order self-consistent approximation to T_{ij} reads

$$T^{(1)}_{ij} = \tilde{T}_{ij} - \tfrac{1}{2} \sum_{l} \left(T^{(1)}_{il} S_{lj} + S_{il} T^{(1)}_{lj}\right) . \tag{3}$$

Notice the linear coupling among the $T^{(1)}_{ij}$'s, which amounts to a sum to infinite order in S having the same form as Eq. (2) (i.e., with terms $S^{m}_{il} \tilde{T}_{lk} S^{n}_{kj}$). However, the coefficients of the second-order and higher-order terms of Eqs. (2) and (3) are not the same and, therefore, $T^{(1)}_{ij}$ differs from the exact result T_{ij}, except in some particular cases (e.g., if $[S, \tilde{T}] = 0$). In spite of this, the solution of Eq. (3) always satisfies an important sum rule, namely, $\mathrm{Tr}(T^{(1)}) = \mathrm{Tr}(T)$. In other words, the center of gravity of the electronic spectrum derived from $T^{(1)}_{ij}$ is exact. The electronic density of states (DOS) is thus free from spurious shifts which would cause errors even in quantities like the energy or forces, which are often not very sensitive to the details in the shape of the DOS. In contrast, the sum rule does not hold strictly if only the first-order (or any finite-order) corrections in Eq. (2) are retained. Furthermore, the self-consistent coupling among the $T^{(1)}_{ij}$'s in Eq. (3) provides a more detailed account of the local geometrical and chemical configuration of the system, since the overlap corrections to a given hopping $T^{(1)}_{ij}$ or energy level $\varepsilon^{(1)}_{i} = T^{(1)}_{ii}$ also involve the environment of the surrounding orbitals l through $T^{(1)}_{il}$ and $T^{(1)}_{lj}$. Such effects are expected to be important particularly for complex systems (e.g., close to a surface or defect) where atoms having different local environments interact.

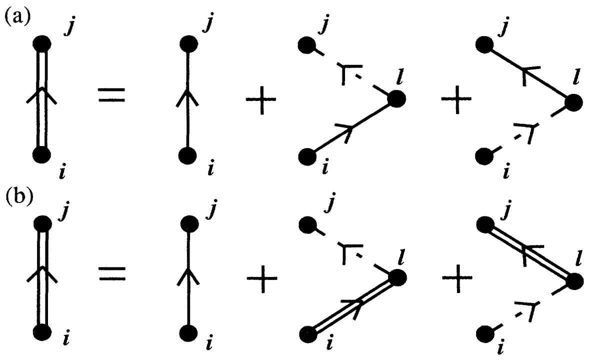

FIG. 1. Diagrammatic representation of overlap interactions for single-particle matrix elements: (a) Equation (2) to first order in S_{ij}, and (b) the corresponding self-consistent equation (3). The double (single) lines represent the orthogonal (nonorthogonal) matrix elements T_{ij} ($\tilde{T}_{ij}$) and the dashed lines the overlap integrals S_{ij}.

Equation (3) can be improved systematically by taking into account higher-order diagrams. The coefficients weighting each of these diagrams are determined by requiring agreement between the self-consistent equation and the exact result [Eqs. (1) and (2)] to the corresponding order in S. The second-order self-consistent approximation to T_{ij} is thus given by

$$T^{(2)}_{ij} = \tilde{T}_{ij} - \tfrac{1}{2} \sum_{l} \left(T^{(2)}_{il} S_{lj} + S_{il} T^{(2)}_{lj}\right) + \tfrac{1}{8} \sum_{lm} \left(T^{(2)}_{il} S_{lm} S_{mj} + S_{il} S_{lm} T^{(2)}_{mj} - 2 S_{il} T^{(2)}_{lm} S_{mj}\right) . \tag{4}$$

Notice that, in contrast to Eq. (2), the sum of the coefficients of the second-order contributions is zero in Eq. (4). The same holds for higher-order terms. This improves considerably the convergence to the exact result and particularly ensures that the exact trace is preserved.[14,15]

As a first application of our theory and in order to demonstrate its accuracy, we calculate the band structure of paramagnetic Ni, as an example of a transition metal (TM), and the band structure of Si, as an example of a semiconductor. Notice that this is one of the most critical tests of such a theory, since the electronic spectrum is known to be very sensitive to the value of the interaction parameters. For the calculations, realistic parameters $\tilde{T}_{ij}$ and overlaps S_{ij} are used, as reported in Ref. 16 (Ni) and Ref. 17 (Si). In Fig. 2 results for Ni are shown, which have been obtained by using the orthogonal parameters $T^{(1)}_{ij}$ derived from the simplest self-consistent approximation [Eq. (3)]. Hoppings $T^{(1)}_{ij}$ beyond fourth-nearest neighbors (NN) have been neglected. The fit to *ab initio* calculations,[16] which includes overlap effects exactly,

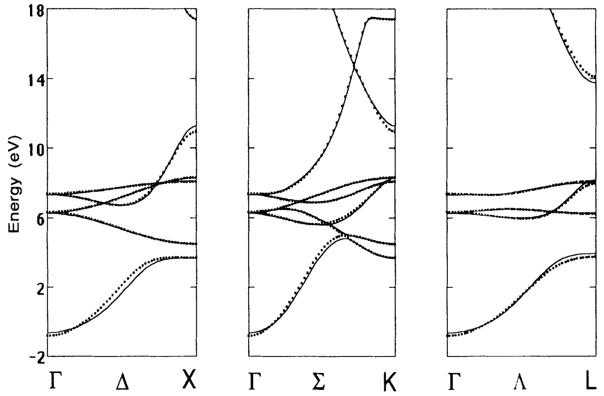

FIG. 2. Band structure of Ni (paramagnetic solution, fcc structure). The solid curves are obtained by using the orthogonal parameters $T^{(1)}_{ij}$ given by the first-order self-consistent equation (3). Hoppings beyond fourth neighbors were neglected. The dotted curves correspond to *ab initio* results (Ref. 16) including overlap effects exactly.

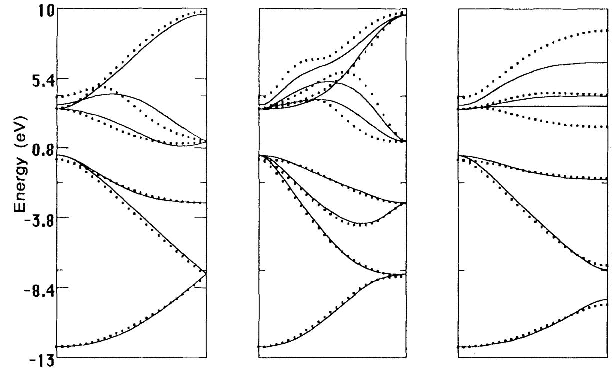

FIG. 3. Band structure of Si (diamond structure). The solid curves are obtained by using the orthogonal parameters $T_{ij}^{(2)}$ given by the second-order self-consistent equation (4). Hoppings beyond fifth neighbors were neglected. The dotted curves correspond to *ab initio* results (Ref. 17) including overlap effects exactly.

is also given for the sake of comparison. The excellent agreement between the outcome of Eq. (3) and the exact result reveals the power of the self-consistent approach. The root-mean-square error σ ranges from $\sigma \simeq 0.1$ eV for the (100) direction to $\sigma \simeq 0.2$ eV for the (111) direction. In contrast, retaining only the first few terms in Eq. (2) yields very poor results ($\sigma \simeq 4$ eV). One therefore concludes that self-consistency is crucial for an accurate account of overlap interactions from a local point of view.

It is interesting to take advantage of the local formulation in order to gain new physical insight into the role of overlap effects on the electronic properties and different NN interactions. For instance, taking into account $T_{ij}^{(1)}$ only up to second NN (i.e., up to the range of the interactions $\tilde{T}_{ij}$ and S_{ij}) (Ref. 16) yields fairly good *d* bands but large discrepancies in the *sp* states (e.g., ~ 2 eV at the Γ point). The inclusion of third NN $T_{ij}^{(1)}$ in Eq. (3) produces already a quite good band structure with almost perfect *d* bands. Only minor quantitative discrepancies are left in the *sp* bands (e.g., ~ 0.4 eV at the Γ point), which are removed in every important respect by including the fourth NN $T_{ij}^{(1)}$ in the calculation (see Fig. 2). The fact that the overlap effects can be grasped as a spatially limited change in the interactions, which depends on the specific local environment of the atoms, is of considerable practical and conceptual importance. This contrasts with Eq. (1) which seems to involve infinitely long-ranged interactions.

Results for Si are shown in Fig. 3, which have been calculated by using the parameters $T_{ij}^{(2)}$ obtained from the second-order self-consistent equation (4). Hoppings beyond fifth NN have been neglected. Notice that the valence bands are very accurately given ($\sigma \simeq 0.16$ eV). However, somewhat larger quantitative discrepancies are present in the conduction bands ($\sigma \simeq 0.6$ eV). These are related to the more delocalized character of the *sp* orbitals of Si, which causes the interactions between more distant neighbors to be non-negligible. In fact, third NN interactions $\tilde{T}_{ij}$ and overlaps S_{ij} are involved already in the nonorthogonal fit.[17] A higher accuracy in the conduction bands could be achieved by including further NN interactions $T_{ij}^{(2)}$ in the calculations. It is worth it to mention that the $T_{ij}^{(1)}$ given by Eq. (3) already yield accurate valence bands and is therefore a very good approximation for problems where mainly the occupied states are relevant (e.g., total-energy calculations, forces).

As application of the theory to complex systems we have solved Eqs. (3) and (4) for small Ni and Si clusters, which are interesting problems on their own and for which the overlap effects on the single-particle energy spectrum can also be calculated exactly using Eq. (1). Notice that the fact that Eqs. (3) and (4) provide very accurate results for the electronic structure of periodic crystals, does not necessarily mean that this is also the case for complex nonperiodic systems, where an interplay between different local environments is present. The electronic DOS of Ni_{13} (paramagnetic) and Si_{13} with fcc-

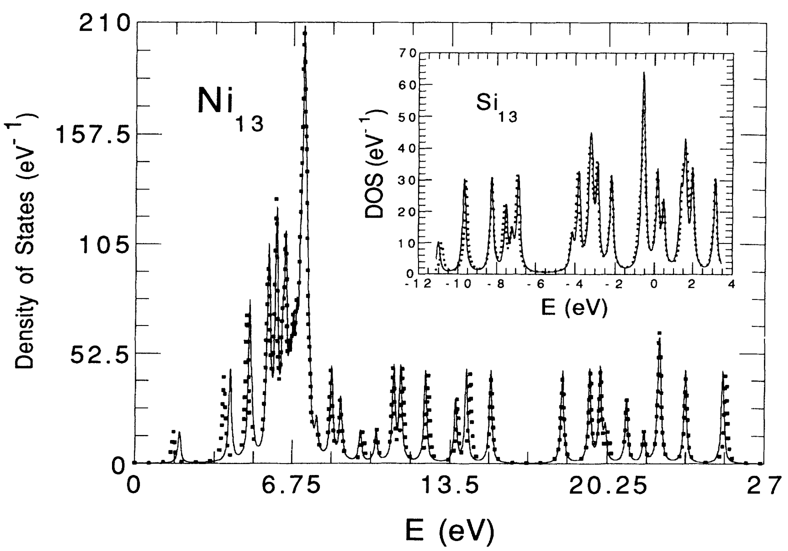

FIG. 4. Density of states (DOS) of Ni_{13} (paramagnetic solution, fcc-like structure). The solid curve is calculated using the orthogonal parameters $T_{ij}^{(1)}$ obtained by solving the first-order self-consistent equation (3) for the cluster environment. In the inset the DOS of Si_{13} (fcc-like structure) is given. Here the solid curve is calculated using the orthogonal parameters $T_{ij}^{(2)}$ obtained from Eq. (4). The dotted curves refer, in both cases, to results including overlap effects exactly. A Lorentzian width $\gamma = 0.05$ eV was used to broaden the cluster energy levels.

like structure are shown in Fig. 4. In both cases our results are in excellent agreement with the exact ones [$\sigma(\mathrm{Ni}_{13}) \simeq 0.07$ eV, $\sigma(\mathrm{Si}_{13}) \simeq 0.06$ eV]. This is remarkable, particularly taking into account the richness of the energy-level structure of the clusters. Once more, the key to the quality of our calculations is the self-consistency between the $T_{ij}^{(1,2)}$ for the characteristic local environment of the system under study. Neither the first few terms of Eqs. (2) nor the use of bulk T_{ij} are adequate approximations, an exception being the d bands of TM. Interestingly, the approximations work better and are easier to solve for low-dimensional systems than for three-dimensional extended systems. This brings additional advantages for many relevant applications.

Concerning the efficiency of our local approach, notice that, as discussed before, the changes in the local environment of the atoms result in changes of the interaction parameters which are of limited spatial extension. For the applications one usually only needs to calculate the overlap effects on a small number of parameters corresponding to atoms close to the defect, interface or adsorbate under study. The size of problem remains thus manageable even for extended systems. Furthermore, it can be shown that the quadratic forms $Q^{(1,2)}(T)$ obtained by integrating Eqs. (3) and (4) with respect to $T_{ij}^{(1,2)}$ are positive definite.[18] Therefore, Eqs. (3) and (4) always have a unique solution which can be obtained by minimizing $Q^{(1,2)}$ using iteration methods in *at most N* steps, where N is the number of unknowns. In our case, the use of the conjugate-gradient method is particularly efficient since analytic expressions for the intermediate line minimizations can be given. Each iteration involves of the order of $N^{3/2}$ operations. In practice, the actual number of iterations n is much smaller than N (typically $n \simeq N/20$). Moreover, for structural optimizations (e.g., surface relaxation, chemisorption, etc.), the solution of a previously calculated geometry provides an excellent guess which yields convergence for very small n.[19]

In conclusion, we have presented a simple, efficient and accurate method of determining locally the interaction matrix elements corresponding to an orthogonal basis in terms of the interaction parameters in a more localized nonorthogonal basis. This theory combines the advantages of orthogonality with the transferability of the nonorthogonal approach and should, therefore, serve as a basis for the study of a wide variety of electronic and structural properties of complex systems.

Helpful discussions with Professor L. C. Balbás are gratefully acknowledged. We also thank Professor P. W. Anderson and Professor W. A. Harrison for their comments on the manuscript. This work has been supported by CONACyT Mexico (Grant No. 0932-E9111), Junta de Castilla y León (Spain), Acciones Integradas Hispano-Alemanas, and SFB 341 of the Deutsche Forschungsgemeinschaft.

---

[1] R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988); N. Binggeli, J.L. Martins, and J.R. Chelikowsky, *ibid.* **68**, 2956 (1992).

[2] For reviews see, for instance, M.W. Finnis, A.T. Paxton, D.G. Pettifor, A.P. Sutton, and Y. Ohta, Philos. Mag. A **58**, 143 (1988); L.M. Falicov, in *Recent Progress in Many Body Theories*, edited by E. Pajanne and R. Bishop (Plenum, New York, 1988), Vol. I, p. 275.

[3] L. Goodwin, A.J. Skinner, and D.G. Pettifor, Europhys. Lett. Phys. **9**, 701 (1989); D.G. Pettifor, Phys. Rev. Lett. **63**, 2480 (1989).

[4] R.H. Victora and L.M. Falicov, Phys. Rev. Lett. **55**, 1140 (1985); C. Chen, *ibid.* **64**, 2176 (1990).

[5] C.Z. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. Lett. **66**, 189 (1991).

[6] G.M. Pastor, S.L. Reindl, and K.H. Bennemann, Phys. Rev. Lett. **67**, 1142 (1991).

[7] W.D. Bullett, *Solid State Physics* (Academic, London, 1980), Vol. 35, pp. 129ff, and references therein.

[8] W.H. Adams, J. Chem. Phys. **34**, 89 (1961); **37**, 2009 (1962); Phys. Rev. Lett. **32**, 1093 (1974).

[9] P.W. Anderson, Phys. Rev. Lett. **21**, 13 (1968); Phys. Rev. **181**, 25 (1969).

[10] W.A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[11] M. van Schilfgaarde and W.A. Harrison, Phys. Rev. B **33**, 2653 (1986).

[12] R. Riedinger *et al.*, Phys. Rev. B **39**, 13 175 (1989).

[13] For simplicity we restrict ourselves here to the Hamiltonian single-particle matrix elements, though the following also applies to other single-particle operators. Many-body interactions are briefly discussed below.

[14] Higher-order self-consistent approximations are easy to obtain. There is, however, no indication that going beyond Eq. (4) is necessary to obtain accurate results, at least for transition-metal and semiconductor systems.

[15] Using these ideas, one can derive self-consistent equations for the Coulomb-interaction integrals V_{ijlm} in the orthogonal basis. For instance, the first-order self-consistent approximation reads $V_{ijlm}^{(1)} = \tilde{V}_{ijlm} - \frac{1}{2}\sum_n(\tilde{S}_{in}V_{njlm}^{(1)} + \tilde{S}_{jn}V_{inlm}^{(1)} + V_{ijnm}^{(1)}\tilde{S}_{nl} + V_{ijln}^{(1)}\tilde{S}_{nm})$. Results for the environment dependence of V_{ijlm} will be reported elsewhere.

[16] D.A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[17] L.F. Mattheiss and J.R. Patel, Phys. Rev. B **23**, 5384 (1981).

[18] For instance, from Eq. (3) one obtains $Q^{(1)}(T) = \frac{1}{2}\mathrm{Tr}\{T^2(1+S)\} - \mathrm{Tr}\{\tilde{T}T\}$.

[19] Further details will be published elsewhere.