

# Localized orbital description of electronic structures of extended periodic metals, insulators, and confined systems: Density functional theory calculations

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We present a simple and general method for construction of localized orbitals to describe an electronic structure of extended periodic metals and insulators as well as confined systems. Spatial decay of these orbitals is found to exhibit exponential behavior for insulators and power law for metals. While these orbitals provide a clear description of bonding, they can be also used to determine polarization of insulators. Within density functional theory, we illustrate applications of this method to crystalline aluminium, copper, silicon,  $\text{PbTiO}_3$ , and molecules, such as ethane and diborane.

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Localized orbitals, such as Wannier functions,<sup>1</sup> have played an important role in many aspects of quantum mechanical description of electrons in solids and molecules. They highlight atomic character of electrons<sup>2</sup> and elucidate the nature of bonding. Their spatial localization makes them useful as basis functions for efficient calculations of electronic structure that scale linearly with system size.<sup>3-5</sup> They are often useful in the construction of lattice model Hamiltonians for structural transitions<sup>6</sup> as well as strongly correlated systems.<sup>7</sup> Wannier functions are intimately related to geometric phases of Bloch electron<sup>8,9</sup> and electric polarization of insulators.<sup>10,11</sup> The recent surge of interest in Wannier functions (WFs) is due to their use in modeling transport<sup>12</sup> and electric field dependent properties of periodic solids.

Many schemes for construction of localized or Wannier orbitals have been presented over the last four decades. To name a few, early works of Foster and Boys<sup>13</sup> were based on maximizing the dipole moment matrix elements between orthonormal orbitals making their centroids maximally apart from each other, followed by Reudenberg's<sup>14</sup> approach of maximizing the orbital self-repulsion energies. Kohn presented a scheme<sup>2</sup> for arriving at exponentially localized real orthonormal WFs through a variational principle for total energy. Maximally localized WFs (MLWF) (Ref. 15) were introduced by Marzari and Vanderbilt that minimize the variance of position operator  $\vec{r}$ , in a given subspace of states. For example, orbitals maximally localized in a spatial direction  $\alpha$  (hermaphrodite orbitals)<sup>16</sup> are eigenfunctions of position operator  $r_\alpha$  in the given subspace. As different components of  $\vec{r}$  do not commute when projected into a subspace, MLWFs are obtained through numerical minimization of variance of  $\vec{r}$  used as a measure of localization. MLWFs have been generalized to the cases of entangled bands<sup>17</sup> and to atom-centered orbitals.<sup>18</sup>

WFs are Fourier transform of Bloch functions:  $W(\mathbf{r}) = \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{\mathbf{k}}(\mathbf{r})$ . Due to freedom in  $\mathbf{k}$ -dependent phase factor accompanying  $\psi_{\mathbf{k}}$ , WFs are nonunique. Smoothness of these phases determine localization properties of WFs. MLWFs in one dimension can be obtained simply (*without* a variational calculation) through construction of Bloch states that are smooth (generated using parallel transport along  $\mathbf{k}$ ) and periodic in  $k$  space.<sup>9</sup> Generalization of this idea to three dimen-

sions is not readily possible, as the smoothness and periodicity of Bloch states as a function of  $k_\alpha$  achieved through parallel transport along one direction is disturbed by that along another direction in  $k$  space. Here, we provide a solution by connecting Bloch states at different  $\mathbf{k}$ 's by parallel transport along paths that run *outside* the  $\mathbf{k}$  space. Resulting Bloch functions are periodic and optimally smooth in all directions in  $k$  space, whose Fourier transform yields well localized WFs. It is efficient and simple because it avoids a variational calculation and issues of local minima. Its versatility is demonstrated through applications to insulators, metals and molecules.

In the first step of this method, we develop an *auxiliary subspace* of highly localized orthonormal orbitals with desired symmetry properties described by (a) center of the orbital (Wyckoff site)  $\{\tau_\kappa\}$  and (b) irreducible representation (irrep) of its site symmetry group according to which it transforms.<sup>2,19</sup> This choice can be guided through symmetry analysis of Bloch states<sup>6,8,20</sup> in the *physical subspace* of occupied states. For simplicity, we use Gaussian form for the radial part and a spherical harmonic corresponding to the irrep of localized orbitals:

$$\Psi_\mu(\mathbf{R}, \mathbf{r}) = (\beta/2\pi)^{3/2} e^{-\beta|\mathbf{r} - \tau_\kappa - \mathbf{R}|^2} Y_{lm}(r - \tau_\kappa - R), \quad (1)$$

where  $\beta$  determines the width of the Gaussian,  $\mathbf{R}$  is a direct space lattice vector, and  $\mu$  is an orbital index.  $\beta$  is chosen to be large enough to keep orbitals in neighboring unit cells orthogonal. The cell periodic part  $v_{\mu\mathbf{k}}$  of Bloch functions spanning the auxiliary subspace is given by Fourier transform:

$$\langle \mathbf{r} | v_{\mu\mathbf{k}} \rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})} \Psi_\mu(\mathbf{R}, \mathbf{r}). \quad (2)$$

We note that  $\{\langle \mathbf{r} | v_{\mu\mathbf{k}} \rangle\}$  are smooth as a function of  $\mathbf{k}$  and satisfy  $|v_{\mu\mathbf{k}}\rangle = |v_{\mu\mathbf{k}+\mathbf{G}}\rangle$ ,  $\mathbf{G}$  being a reciprocal lattice vector. Localized functions constructed in this scheme are found to depend mainly on the geometric properties of the auxiliary subspace (determined largely by symmetries) and not on the details of functions defining it.

In the second step, we perform a unitary transformation of Bloch states in the physical subspace (e.g., energy eigenfunc-

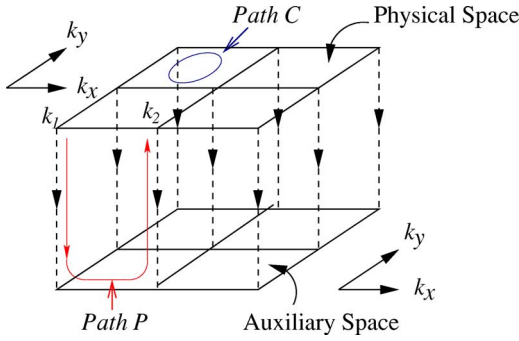


FIG. 1. (Color online) Two horizontal planes are used to display physical and auxiliary subspaces, in which the member functions are parametrized with  $k_x$  and  $k_y$ . Dashed lines indicate paths connecting states at a given  $\mathbf{k}$  in physical subspace with those in the auxiliary subspace.

tions of occupied states), such that the open path<sup>21</sup> nonabelian geometric phases between states in physical and auxiliary subspaces at fixed  $\mathbf{k}$  vanish. Overlap matrix  $S_{\mu\nu}^{\mathbf{k}} = \langle v_{\mu\mathbf{k}} | u_{\nu\mathbf{k}} \rangle$ , where  $|u_{n\mathbf{k}}\rangle$  is cell periodic part of energy, an eigenstate, relates to geometric phase matrix  $\Gamma_{\mathbf{k}}$  through

$$S^{\mathbf{k}} = R_{\mathbf{k}} e^{i\Gamma_{\mathbf{k}}}, \quad (3)$$

where  $R$  is a positive definite Hermitian matrix. Determination of  $R$  and  $\Gamma_{\mathbf{k}}$  is accomplished using singular value decomposition of  $S$ :

$$S^{\mathbf{k}} = U_{\mathbf{k}} \Sigma_{\mathbf{k}} V_{\mathbf{k}}^{\dagger}, \quad (4)$$

where  $\Sigma_{\mathbf{k}}$  is a diagonal matrix with non-negative singular values in its diagonal. Vanishing of singular value(s) at some  $\mathbf{k}$  signals a nonoptimal choice of symmetries of localized orbitals in the auxiliary subspace and the need for correction. Using Eq. (4),  $R_{\mathbf{k}} = U_{\mathbf{k}} \Sigma_{\mathbf{k}} U_{\mathbf{k}}^{\dagger}$  and  $e^{i\Gamma_{\mathbf{k}}} = U_{\mathbf{k}} V_{\mathbf{k}}^{\dagger}$ . A unitary transformation on the  $\{u_{n\mathbf{k}}\}$  given by a matrix  $M_{\mathbf{k}} = (U_{\mathbf{k}} V_{\mathbf{k}}^{\dagger})^*$  transforms the overlap matrix  $S^{\mathbf{k}}$  to a Hermitian form,

$$\tilde{S}^{\mathbf{k}} = S^{\mathbf{k}} (V_{\mathbf{k}} U_{\mathbf{k}}^{\dagger}) = U_{\mathbf{k}} \Sigma_{\mathbf{k}} U_{\mathbf{k}}^{\dagger},$$

corresponding to vanishing geometric phases.

A sketch in terms of paths that connect physical and auxiliary subspaces (shown in Fig. 1) enables an understanding of our method. Closed paths parametrized by  $\mathbf{k}$ , such as  $C$ , in the physical subspace can have nontrivial geometric phases which forbid construction of smooth functions by parallel transport along  $\mathbf{k}$  within the physical subspace. In the present method, we make use of paths, labeled as  $P$ , to connect states at two  $\mathbf{k}$ 's in the physical space. For  $\mathbf{k} = \text{constant}$  segments of path  $P$  (dashed lines), geometric phases are made to vanish. Second, geometric phases along any closed path parametrized by  $\mathbf{k}$  in the auxiliary subspace vanish. Hence, Bloch functions in the physical subspace transformed with  $M_{\mathbf{k}}$  have a single valued and periodic phase as a function of  $\mathbf{k}$ .

We include occupation numbers  $f_{n\mathbf{k}}$  while transforming energy eigenfunctions and obtain

$$|\tilde{u}_{\mu\mathbf{k}}\rangle = \sum_j M_{\mu j} |u_{j\mathbf{k}}\rangle f_{n\mathbf{k}}^{1/2}, \quad (5)$$

which are periodic in  $\mathbf{k}$  by construction and the random phases accompanying  $\{u_{n\mathbf{k}}\}$  are filtered out in this procedure. Localized orbitals are obtained by Fourier transforming  $\{\tilde{u}_{\mu\mathbf{k}}(\mathbf{r})\}$ :

$$\langle \mathbf{r} | \Phi_{\mu}(\mathbf{R}) \rangle = \frac{\Omega}{(2\pi)^3} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R})} \langle \mathbf{r} | \tilde{u}_{\mu\mathbf{k}} \rangle, \quad (6)$$

where  $\Omega$  is the unit-cell volume. Localization of  $|\Phi_{\mu}(\mathbf{R})\rangle$  is determined by the ‘‘smoothness’’ of  $\{\tilde{u}_{\mu\mathbf{k}}(\mathbf{r})\}$ , which depends on the precise location of center and symmetry properties of localized orbitals in the auxiliary subspace. A quantitative idea of the *smoothness* is obtained with the Berry connection matrix  $B_{\alpha}(k)$ :

$$B_{\alpha}^{\mu\nu}(k) = -\text{Im} \langle \tilde{u}_{\mu\mathbf{k}} | \frac{\partial}{\partial k_{\alpha}} | \tilde{u}_{\nu\mathbf{k}} \rangle, \quad (7)$$

and its Fourier components. If the matrix  $B_{\alpha}(k)$  is diagonal and its diagonal entries are constant as a function of  $k_{\alpha}$  (it has vanishing Fourier components for  $\mathbf{R} \neq 0$ ),  $\Phi_{\mu}$  are maximally localized in  $\alpha$  direction.<sup>9,16</sup> For the systems studied in this work, diagonal elements of  $B$  are found to be constant as a function of  $k$ , indicating good localization properties of  $\Phi_{\mu}$ .

We note that functions  $|\Phi_{\mu}(\mathbf{R})\rangle$  are *not* maximally localized<sup>15</sup> by construction. However, if desired, the MLWFs can be readily obtained through a single step of joint diagonalization<sup>22</sup> of the three components of position operators in  $\Phi$ -basis:

$$\langle r_{\alpha} \rangle_{\mu, \mu', R_1, R_2} = \int_{\Omega_{Nk_{\alpha}}} \Phi_{\mu}^*(\mathbf{R}_1, \mathbf{r}) r_{\alpha} \Phi_{\mu'}(\mathbf{R}_2, \mathbf{r}) d\mathbf{r}. \quad (8)$$

This will be particularly useful for disordered systems and macromolecules. The electronic part of electric polarization is obtained using:

$$P_{\alpha}^{\text{el}} = \frac{q}{\Omega} \sum_{\mu} \langle \Phi_{\mu}(\mathbf{R} = \mathbf{0}) | r_{\alpha} | \Phi_{\mu}(\mathbf{R} = \mathbf{0}) \rangle. \quad (9)$$

Inclusion of occupation numbers in Eq. (5) ensures a simple and general form for density matrix  $\rho(r, r') = \sum_{R, \mu} \langle r | \Phi_{\mu}(R) \rangle \times \langle \Phi_{\mu}(R) | r' \rangle$ . As the present analysis at  $\mathbf{k}$  is decoupled from that at other  $\mathbf{k}$ 's, it applies equally well to simple, compound, and entangled bands, and can be performed efficiently on a parallel computer. For molecules or confined systems treated within periodic boundary conditions, it can be readily applied using a single  $\mathbf{k} = (000)$  point; it applies equally well to confined systems treated with open boundary conditions. In the present scheme, construction of atom-centered orbitals<sup>18</sup> for covalent systems necessitates expansion of the physical subspace to include antibonding bands. It is somewhat similar to physically intuitive derivation of WFs in Ref. 23.

We illustrate our method within density functional theory through applications to insulators, metals, and molecules. The energy eigenstates, which are the main inputs to our method, are calculated using ABINIT implementation<sup>24</sup> of density functional theory and norm-conserving pseudopoten-

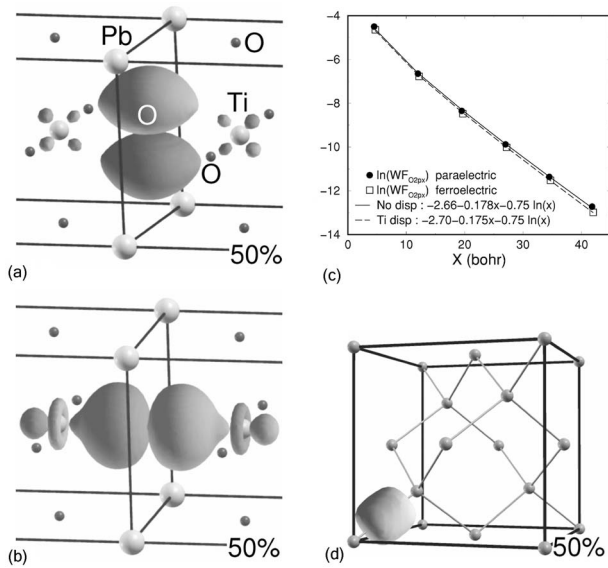


FIG. 2. (a) and (b)  $2p_y$  and  $2p_x$  orbitals, respectively, of a bridging oxygen in  $\text{PbTiO}_3$ . (c) shows the nature of decay of the  $2p_x$  orbital shown in (b) for the paraelectric phase. (d) A bond centered orbital representing the Si-Si  $\sigma$ -bond in bulk Si.

tials. We use Monkhorst–Pack meshes (finer than a  $9 \times 9 \times 9$  mesh) of  $k$  points to sample Brillouin zones. Iso-surfaces of localized orbitals (indicating isovalue as percentage of its maximum in figures) have been generated using a visualization software XcrystDen.<sup>25</sup>

For  $\text{PbTiO}_3$  in the cubic perovskite structure, symmetry of occupied bands implies the choice of atom-centered orbitals: Pb centered ( $s$  and  $d$  like), Ti centered ( $s$  and  $p$  like), and O centered ( $s$  and  $p$  like). Oxygen centered localized orbitals with  $p$  symmetry form two groups: (1) Those perpendicular to the  $-\text{O}-\text{Ti}-\text{O}-$  chain [Fig. 2(a)], and (2) those along the  $-\text{O}-\text{Ti}-\text{O}-$  chain [Fig. 2(b)]. A former has  $\pi$ -like overlap with  $d_{xy}$  orbital of Ti and a variance of  $1.44 \text{ \AA}^2$ , while the latter has  $\sigma$ -like overlap with  $d_{z^2}$  orbital of Ti and a smaller variance of  $1.14 \text{ \AA}^2$ . For an O-centered orbital with  $s$  symmetry, we get a variance of  $0.54 \text{ \AA}^2$  (compared with  $0.52 \text{ \AA}^2$  of Ref. 26). We determined Born effective charge ( $Z^*$ ) of Ti using  $Z^* = \Omega \Delta P_\alpha / \Delta d_\alpha$ , where  $\Delta d_\alpha$  is a small displacement of Ti atom that changes the net polarization ( $P_\alpha = P_\alpha^{\text{ion}} + P_\alpha^{\text{el}}$ ) by  $\Delta P_\alpha$ . Our estimate of  $Z^*(\text{Ti}) = 7.02$  agrees well with a linear response calculation,<sup>24</sup> with contribution from each O-centered  $p$  orbital in groups (1) and (2) of 1.6 and 0.8, respectively. Our estimate of  $Z^*(\text{Pb}) = 3.86$ , also in good agreement with the linear response result, has a contribution of 1.4 from O-centered orbitals in Ti–O planes. Spatial decay of an O-centered orbital in group (2), shown in Fig. 2(c), exhibits a power law times exponential form.<sup>2</sup> The power-law exponent obtained from a fit is  $-0.75$ , consistent with a theoretical prediction.<sup>27</sup> We confirmed that the diagonal elements of the Berry connection matrix [Eq. (7)] do not change with  $\mathbf{k}$ , indicating individually maximal localization of these orbitals.

For Si in a diamond structure, a covalent semiconductor, we illustrate construction of bond- and atom-centered orbitals corresponding to different choices of subspaces. Symme-

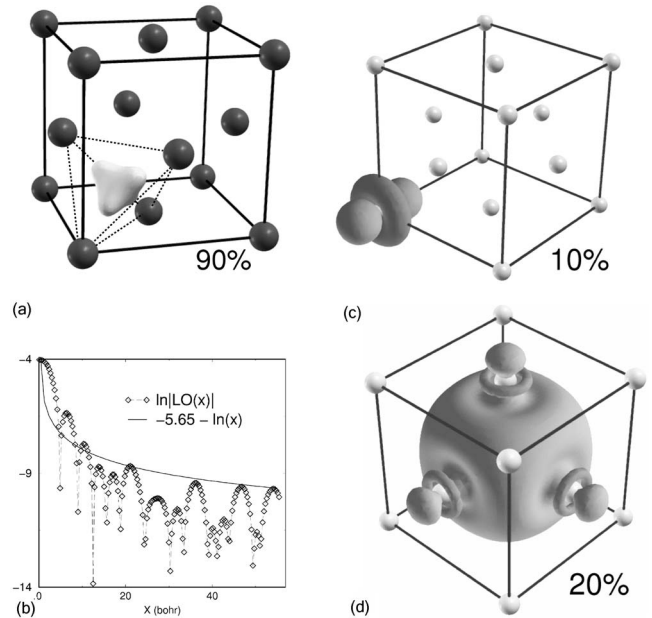


FIG. 3. Localized orbitals of metals: An orbital centered at the tetrahedral site of Al (a), and its spatial decay (b); atom centered LO with  $3d_{2z}$  symmetry (c) and an LO centered at the octahedral site of Cu (d).

tries of Bloch states in the occupied subspace ( $D=4$ ) dictate a choice of bond-centered orbital with full site symmetry. Corresponding bond centered orbitals [shown in Fig. 2(d)] have a variance of  $2.2 \text{ \AA}^2$  (compared with  $2.05 \text{ \AA}^2$  of an MLWF)<sup>15</sup> each. We find that the diagonal elements of Berry connection matrix are indeed constant as a function of  $k$ , implying maximal localization of an orbital individually. In the construction of atom-centered orbitals we use double the number of bands in physical subspace, and atom-centered orbitals with  $s$  and  $p$  symmetry. Our scheme provides two options: (1) treat silicon as a metal [using occupation numbers in Eq. (5)], which generates nonorthonormal atom-centered orbitals that exactly span the occupied subspace, and (2) not use occupation numbers, which generates orthonormal atom-centered orbitals that span the occupied as well as unoccupied states. The former can be important in studies of bonding, whereas the latter could be useful as basis in  $O(N)$  methodology.

We illustrate localized orbitals in metallic systems characterized by multicentered bonding, i.e., sharing of electrons among more than two atoms, with examples of Cu and Al in the face-centered-crystal (fcc) crystal structure. Due to partial occupancy of bands in metals, the dimensionality of auxiliary subspace is taken to be greater than the largest number of occupied bands at any  $\vec{k}$ , the same as the number of energy bands calculated in DFT calculation with temperature smearing used for occupation numbers. In the case of Al, we used (guided by symmetry and singular values) spherically symmetric orbitals centering at the tetrahedral sites  $(1, 1, 1)a/4$  in addition to atom-centered  $s$ -like orbital to construct an auxiliary subspace. From normalization, we find each localized orbital centered at the tetrahedral site [Fig. 3(a)] and the atomic site to be occupied with  $1.2e$  and  $0.6e$ , respectively.

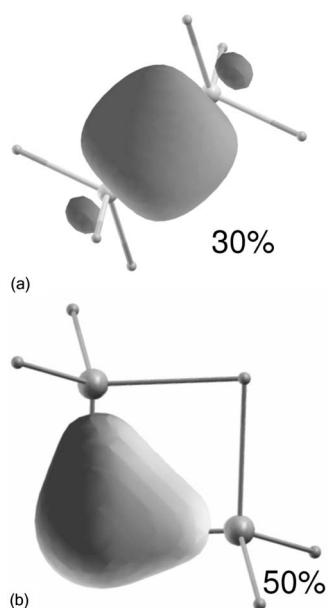


FIG. 4. (a) A bond centered orbital representing the C–C  $\sigma$ -bond in  $C_2H_6$ . (b) The B–H–B three center bond in  $B_2H_6$ .

The former provides four-centered directional bonding among the four Al atoms equidistant from its center. Its spatial decay [shown in Fig. 3(b)] exhibits a power-law decay with an exponent  $-1$ , consistent with earlier calculations<sup>28</sup> in the free electron limit. In the case of Cu, we used atom centered  $s$ - and  $d$ -like orbitals and an  $s$ -like orbital centered at octahedral site  $O=(1, 1, 1)a/2$ . Among atom-centered or-

bitals, a  $d$ -like orbital [Fig. 3(c)] is quite localized and is occupied with  $1.86e$ , while the  $s$ -like orbital is occupied with  $0.69e$ . The orbital centered in the octahedral site [shown in Fig. 3(d)] is occupied with  $1.01e$  providing a six-centered bond, and exhibits slight mixing with atomic  $d$  orbitals. Our results clearly reveal stronger directional bonding in Al than in Cu, which was also concluded from charge density analysis in understanding contrasting mechanical behavior of Al and Cu.<sup>29</sup>

Finally, we demonstrate application of the present scheme to localized orbitals in  $C_2H_6$  and  $B_2H_6$  molecules. In the former, we have used bond-centered orbitals and in the latter, we use bond-centered orbitals for the  $BH_2$  radicals and  $s$ -like orbitals centered on H atoms that bridge the two  $BH_2$  radicals. C–C  $\sigma$ -bonding orbital [Fig. 4(a)] has a variance of  $0.83 \text{ \AA}^2$ , which reduces to  $0.76 \text{ \AA}^2$  after joint diagonalization to obtain an MLWF. Orbitals corresponding to heteropolar C–H  $\sigma$  bonds have their centroids closer to the H atoms. The orbital centered on a bridging H atom of  $B_2H_6$  [shown in Fig. 4(b)] reveals the well-known three-centered bond, and has a variance of  $0.96 \text{ \AA}^2$  each.

In conclusion, we have presented a simple method for construction of well localized orbitals that is applicable to extended metals and insulators as well as finite systems. While demonstrated here for electronic problems, it can be readily used in treatment of phonons. It should be useful for a large number of problems in condensed matter physics.

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