

# Fully-Selfconsistent Electronic-Structure Calculation Using Nonorthogonal Localized Orbitals within a Finite-Difference Real-Space Scheme and Ultrasoft Pseudopotential

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We construct a fully-selfconsistent formalism of *ab initio* electronic-structure calculations, where basis orbitals are localized, nonorthogonal, and given on a real-space *regular* grid. A window function is adopted to optimize localized basis orbitals. As an example, the ground state of diamond crystal is calculated using the ultrasoft pseudopotential.

KEYWORDS: first principle electronic-structure calculation, real space method, order-M method

After the great success of the Car-Parrinello (C-P) method,<sup>1-3)</sup> a new era has begun for *ab initio* electronic-structure calculations, or electronic-structure calculations within the density-functional theory (DFT).<sup>4,5)</sup> The C-P method has been improved in various aspects, one of which is the development of methods for applications to large systems. The C-P scheme is based on the plane-wave basis and soft pseudopotentials<sup>6,7)</sup> or the ultrasoft pseudopotential<sup>8-11)</sup> can actually reduce the number of basis plane waves. In the present C-P scheme, as a result, a typical system size is some hundreds of atoms in a periodic cell for silicon, or approximately one hundred atoms for other elements.

Another important step toward large-scale calculations is the 'order-N' scheme, where the algorithms are designed so that the computational cost is  $O(N)$ , or linearly proportional to the system size  $N$ . Hereafter we denote  $N$  as the number of occupied (valence) one-electron states in a periodic cell for a bulk system. For the 'order-N' scheme, two issues are essential; one is a formulation without explicit orthogonalization or matrix-inversion procedures, because these procedures have  $O(N^3)$  CPU time. Mauri *et al.*<sup>12,13)</sup> overcame this difficulty by introducing a new energy functional in the variational procedure called 'unconstrained minimization' (UM).

The other issue is to construct a localized basis set, because the present C-P scheme consumes  $O(N^2 \log_2 N)$  CPU time for the Fast Fourier Transform (FFT) procedures of all orbitals.<sup>2,3)</sup> To avoid this difficulty, we could use a tight-binding formalism with fixed local basis functions, but the application of local basis functions to fully-selfconsistent treatment is not trivial. Local bases applicable to fully-selfconsistent calculations may be given on a real-space *regular* grid, or on uniform mesh points in a Cartesian coordinate. A DFT calculation with such real-space regular grids is given by Chelikowsky and coworkers<sup>14-16)</sup> and is called 'finite-difference (FD) real-space scheme', where the kinetic-energy operator, or the Laplacian operator, must be a finite difference on real-space grids. In our previous works,<sup>17,18)</sup> we constructed a foundation of the FD real-space scheme with an *exact* FD

formula for the kinetic-energy operator and using a new preconditioning operation, where some results show an excellent agreement with those by the current plane-wave scheme. However, this scheme is based on a global grid mesh in real space and could not be directly applied to the local-basis formulation.

We present in this paper (i) a general formalism of nonorthogonal local bases, applicable to the FD real-space scheme and (ii) a way to construct localized basis orbitals on a real-space regular grid. These are essential to a fully-selfconsistent 'order-N' method. Basic ideas for achieving these goals are, respectively, (i) the UM formulation explicitly using nonorthogonal orbitals, and (ii) a window-function technique for constructing localized basis orbitals. The present method is applied to diamond crystal using the ultrasoft pseudopotential.<sup>8-11)</sup>

First we explain an application of the unconstrained-minimization (UM) technique<sup>12,13)</sup> to nonorthogonal basis sets. In the DFT theory<sup>4,5)</sup> with orthogonal basis orbitals  $\{\psi\}$ , the total electronic energy  $E_{\text{tot}}$  is

$$E_{\text{tot}} \equiv 2 \sum_k^N \langle \psi_k | \hat{T} + \hat{V}_{\text{NL}}^{\text{ion}} | \psi_k \rangle + E_{\text{LHXC}}[n], \quad (1)$$

$$E_{\text{LHXC}}[n] \equiv \int d\mathbf{r} V_{\text{loc}}^{\text{ion}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[n]. \quad (2)$$

Here,  $2N$  is the total (valence) electron number per periodic cell and the charge density  $n(\mathbf{r})$  is defined as

$$n(\mathbf{r}) \equiv 2 \sum_k^N \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}), \quad (3)$$

and the integration  $\int n(\mathbf{r}) d\mathbf{r} = 2\text{Tr}[S] = 2 \sum_k^N S_{kk}$  is always equal to the correct value  $2N$ . The orthogonalization constraint  $S_{ij} \equiv \langle \psi_i | \psi_j \rangle = \delta_{ij}$  should be satisfied in the variational procedure, so this formalism requires an explicit orthogonalization procedure, such as the Lagrange-multiplier technique or the Gram-Schmidt's procedure, which consumes  $O(N^3)$  CPU time. Hereafter

we call this formalism the ‘constrained minimization’.

The UM technique<sup>12,13)</sup> was proposed so as to release the orthogonalization constraint and omit explicit orthogonalization steps in the variational procedure. This fundamental idea is based on a new variational procedure without any explicit orthogonalization procedure, and introduces a new energy functional  $E_{\text{UM}}$

$$E_{\text{UM}} \equiv 2 \sum_{ij}^N A_{ij} \langle \psi_i | \hat{T} + \hat{V}_{\text{NL}}^{\text{ion}} | \psi_j \rangle + E_{\text{LHXC}}[n] + 2\mu\Delta N, \quad (4)$$

$$\Delta N \equiv N - \sum_{ij}^N A_{ij} S_{ij} = \sum_{ij}^N |S_{ij} - \delta_{ij}|^2. \quad (5)$$

Here, the matrix  $A_{ij}$  is defined as  $A_{ij} \equiv 2\delta_{ij} - S_{ji}$  or  $A^t = 2I - S$  and  $I$  is the unit matrix. The charge density is redefined as

$$n(\mathbf{r}) \equiv 2 \sum_{ij}^N A_{ij} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}), \quad (6)$$

and their integration  $\int n(\mathbf{r}) d\mathbf{r}$  is *not necessarily* equal to the correct value  $2N$ . The parameter  $\mu$  must be appropriately chosen, and Mauri *et al.*<sup>12,13)</sup> showed that the minimization of  $E_{\text{UM}}$  leads to the true ground state, when the parameter  $\mu$  is chosen to be larger than the highest occupied level ( $\mu > \epsilon_N$ ).

Here, we comment on the UM formalism. (i) Once the matrix  $A$  is set to be  $A^t = S^{-1}$ , the formalism is equivalent to the ‘constrained minimization’ formalism, and requires a matrix-inversion procedure instead of explicit orthogonalization procedures. (ii) The definition  $A^t \equiv 2I - S$  corresponds to the lowest expansion of the series  $S^{-1} = \{I - (I - S)\}^{-1} = I + (I - S) + (I - S)^2 + (I - S)^3 + \dots$  (iii) The minimization of the term  $2\mu\Delta N$  in the energy functional (4) requires an iterative orthogonalization procedure ( $S_{ij} \rightarrow \delta_{ij}$ ). When orthogonalization is achieved ( $S_{ij} = \delta_{ij}$  thus  $A_{ij} \equiv 2\delta_{ij} - S_{ji} = \delta_{ij}$ ), the minimization of  $E_{\text{UM}}$  is, again, identical to the ‘constrained minimization’ formalism and requires neither explicit orthogonalization procedures nor matrix-inversion procedures. (iv) The quantity  $2\Delta N \equiv 2N - 2 \sum_{ij}^N A_{ij} S_{ij} = 2N - \int n(\mathbf{r}) d\mathbf{r}$  is a deviation of the charge from the correct value, and so one may see that the energy functional (4) works as a ‘ground-canonical’ potential and that the parameter  $\mu$  works as a ‘chemical potential’.

This UM procedure can be generalized to the framework of the localized basis orbitals. We expand the physical orbitals  $\{\psi\}$ , or the valence wavefunctions, into localized basis orbitals  $\{\phi\}$ , just as in the linear combination of atomic orbitals (LCAO) approximation,

$$\psi_i(\mathbf{r}) = \sum_{i'}^M c_{ii'} \phi_{i'}(\mathbf{r}). \quad (7)$$

Here  $\{\phi\}$  are basis orbitals localized in real space and assumed to be centered on atomic sites. The total number of the localized basis orbitals  $\{\phi\}$ ,  $M$ , is not necessarily equal to the number of occupied one-electron states  $N$ . We chose  $M = 2N$  in our test calculation, which is discussed later. When we substitute eq. (7) into eqs. (4),

(5) and (6), we obtain, respectively,

$$E_{\text{UM}} \equiv 2 \sum_{ij}^M B_{ij} \langle \phi_i | \hat{T} + \hat{V}_{\text{NL}}^{\text{ion}} | \phi_j \rangle + E_{\text{LHXC}}[n] + 2\mu\Delta N, \quad (8)$$

$$\Delta N \equiv N - \sum_{ij}^M B_{ij} S_{ij}, \quad (9)$$

and

$$n(\mathbf{r}) \equiv 2 \sum_{ij}^M B_{ij} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}). \quad (10)$$

Here, matrix  $B_{ij}$  is defined as  $B_{ij} \equiv \sum_{i',j'}^N c_{i'i}^* c_{j'j} A_{i'j'}$  and  $\int n(\mathbf{r}) d\mathbf{r} = 2\text{Tr}[B^t S] = 2 \sum_{ij}^M B_{ij} S_{ij}$ . This procedure is equivalent to that by Hernández *et al.*,<sup>19)</sup> based on the density matrix approach with a model local potential. The only difference in the energy functional is the form of  $B_{ij}$  or a choice of variational parameters in the actual procedure. One should refer to a comment on this point in section IIC of their paper.<sup>19)</sup>

Note that in our actual test calculation with the ultrasoft pseudopotential,<sup>8-11)</sup> the definitions (3), (6) and (10) are also replaced, respectively, by  $n(\mathbf{r}) \equiv 2 \sum_k^N \langle \psi_k | \hat{S}(\mathbf{r}) | \psi_k \rangle$ ,  $n(\mathbf{r}) \equiv 2 \sum_{ij}^N A_{ij} \langle \psi_i | \hat{S}(\mathbf{r}) | \psi_j \rangle$  and  $n(\mathbf{r}) \equiv 2 \sum_{ij}^M B_{ij} \langle \phi_i | \hat{S}(\mathbf{r}) | \phi_j \rangle$ , respectively. Here the operator  $\hat{S}$  is defined<sup>8)</sup> as

$$\langle \phi_i | \hat{S}(\mathbf{r}) | \phi_j \rangle \equiv \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) + \sum_{Inm} Q_{nm}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_j \rangle, \quad (11)$$

where  $I$  indicates an atom, and suffixes  $n$  and  $m$  indicate reference states in an atom. The overlap matrix  $S_{ij}$  is redefined as

$$S_{ij} \equiv \int d\mathbf{r} \langle \phi_i | \hat{S}(\mathbf{r}) | \phi_j \rangle \equiv \langle \phi_i | \phi_j \rangle + \sum_{Inm} q_{nm}^I \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_j \rangle, \quad (12)$$

where  $q_{nm}^I = \int d\mathbf{r} Q_{nm}^I(\mathbf{r})$ . See the original work<sup>8)</sup> for more details.

Second, we explain how to generate localized basis orbitals within the FD real-space scheme. To construct localized orbitals on a real-space regular grid, we adopt a window-function technique, which allows us to optimize the forms of localized basis orbitals instead of fixing them. A localized orbital  $\phi_i$  could be generated from an extended orbital  $\tilde{\phi}_i$  by

$$\phi_i(\mathbf{r}) \equiv w_i(\mathbf{r}) \tilde{\phi}_i(\mathbf{r}). \quad (13)$$

Here, we introduce a *window* function  $w_i$  to localize basis orbitals within a spherical region around an ion. The form of a window function must depend only on the distance from the ion position  $\mathbf{R}$  that the localized orbital belongs to, i.e.,  $w(\mathbf{r}) = w(|\mathbf{r} - \mathbf{R}|) (|\mathbf{r} - \mathbf{R}| > R_L)$ , and is zero outside the local ‘cell’, i.e.,  $w(|\mathbf{r} - \mathbf{R}|) = 0 (|\mathbf{r} - \mathbf{R}| < R_L)$ . The parameter  $R_L$  is the radius of the local cell.

The implementation of a window function guarantees the locality of  $\phi_i$  in a spherical local-cell region ( $|\mathbf{r} - \mathbf{R}| < R_L$ ) and satisfies the (Dirichlet) boundary condition. The resultant variational procedure should be achieved with respect to  $\{\bar{\phi}\}$  and  $\{c_{ii'}\}$ . The variations with respect to the orbitals  $\{\bar{\phi}\}$  correspond to the optimization of the local basis function on a real-space regular grid and those with respect to the coefficients  $\{c_{ii'}\}$  correspond to the determination of eigen states. Though  $\bar{\phi}$  is, in principle, an extended function, its components in the outer region ( $|\mathbf{r} - \mathbf{R}| > R_L$ ) do not contribute to the total energy and so we can neglect these components in actual computational procedures.

The energy variation with respect to  $\bar{\phi}$  is reduced to

$$\frac{\delta E}{\delta \bar{\phi}_i(\mathbf{r})} = \frac{\delta \phi_i(\mathbf{r})}{\delta \bar{\phi}_i(\mathbf{r})} \frac{\delta E}{\delta \phi_i(\mathbf{r})} = w_i(\mathbf{r}) \frac{\delta E}{\delta \phi_i(\mathbf{r})}, \quad (14)$$

and guarantees the locality of  $\bar{\phi}$  if the initial functions of  $\{\bar{\phi}\}$  are localized. In our calculation, we use the ultrasoft pseudopotential, where  $(\hat{T} + \hat{V}_{\text{NL}}^{\text{ion}})|\phi\rangle$  is not localized in a local cell. Therefore this formalism of the window function is essential to optimize the localized basis orbitals on a regular grid. The window-function technique is also advantageous in force calculations, which is important in a molecular-dynamics simulation. Because a localized orbital  $\phi$  depends on the position of the ion  $\mathbf{R}$  only through the window function  $w(|\mathbf{r} - \mathbf{R}|)$ , the derivatives of orbitals with respect to positions of ions are reduced to

$$\frac{\partial \phi_i(\mathbf{r})}{\partial \mathbf{R}} = \frac{dw_i(\mathbf{r})}{d\mathbf{R}} \bar{\phi}_i(\mathbf{r}), \quad (15)$$

which could calculate the Pulay force straightforward.

We must note that the present formulation is an intermediate scheme between a tight-binding formalism and a fully-selfconsistent (DFT) formalism with a complete basis set, in the sense that, if we fix basis orbitals  $\{\phi\}$  and the charge density  $n(\mathbf{r})$ , the formalism is reduced to the tight-binding formulation. One interesting application of the present formalism is a calculation with ‘partially fixed’ basis orbitals. For many calculations, such as surface structures and defects in solids, almost all atoms are the same as in a bulk system, except those near a surface or a defect. In such a ‘bulk’ region, localized basis orbitals could be fixed to be ‘bulk’ states in a good approximation. This saves CPU time and memory space for computation. Even in this case, the calculation can be fully-selfconsistent, because the Hamiltonian is exactly equal to that of the DFT with no parameters.

We tested the present formalism numerically on the ground state of diamond crystal, using the ultrasoft pseudopotential<sup>8-11</sup> and the local-density approximation (LDA) with the Perdew-Zunger exchange-correlation potential,<sup>20</sup> and used the cubic supercell containing 8 atoms, where the edge length of a periodic cell  $L$  is  $L = 6.727$  atomic unit (a.u.). We use the double-grid technique in the ultrasoft pseudopotential,<sup>8-11</sup> where the spacings of the real-space grid  $h$  are  $h = 0.42$  a.u. for orbitals and  $0.21$  a.u. for the charge density. As in our previous works,<sup>17,18</sup> with the constrained minimization and the FD real-space scheme, the FFT procedures are used

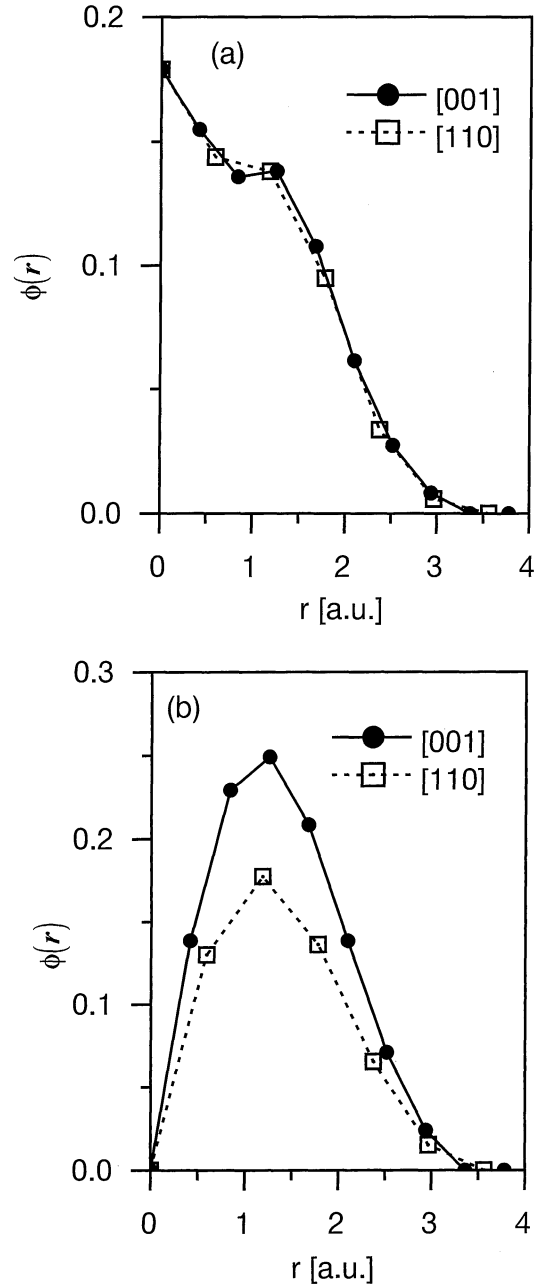


Fig. 1. Localized basis orbitals  $\{\phi\}$  in diamond crystal, as a function of the distance from the atom (atomic unit), optimized by the present variational procedure: (a) initially s-Gaussian (b) initially  $p_z$ -Gaussian. The orbitals  $\{\phi\}$  are normalized.

to generate the potential from the charge density  $n(\mathbf{r})$ . These procedures do not consume CPU time, whereas, in the current plane-wave scheme, the FFT procedures of all orbitals dominate CPU time.

Four localized orbitals  $\phi_i$  for each atom are prepared, and their initial forms are chosen to be (s-,  $p_x$ -,  $p_y$ -,  $p_z$ -) atom-centered Gaussian forms, as those in Hernández *et al.* The basis orbitals are optimized in the variational procedure of eq. (8). The actual forms of s- and  $p_z$ - Gaussians, for instance, are  $\bar{\phi}_s = \exp(-r^2/R^2)$  and  $\bar{\phi}_{p_z} = z \exp(-r^2/R^2)$ , respectively, where the width of Gaussian  $R$  is  $R = 2.018$  a.u. The number of valence orbitals  $\{\psi\}$  for a carbon atom is two, and so the choice of four localized basis orbitals  $\{\phi\}$  per atom corresponds

to  $M = 2N$ . A window function  $w(r)$  is chosen as  $w_i(r) \equiv \cos(\frac{\pi}{2}\frac{r}{R_L})$  inside a local cell ( $r < R_L$ ), and  $w_i(r) \equiv 0$  outside ( $r > R_L$ ). The radius of the local cell  $R_L$  is  $R_L = 3.3635$  a.u.

The resultant ground-state energy per atom  $E$  is  $E = 5.602$  a.u./atom, which agrees satisfactorily with the value of  $E = 5.617$  a.u./atom in our previous work,<sup>11,18)</sup> calculated using the constrained minimization and the FD real-space scheme. For comparison, we also calculated using 'fixed' local basis orbitals, where localized orbitals  $\{\phi\}$  are fixed to be the initial Gaussian forms and only coefficients  $\{c_{ii'}\}$  are optimized in the variational procedure. The resultant ground state energy  $E = 5.204$  a.u./atom is worse than the result calculated with optimized  $\{\phi\}$ . Therefore, the optimization of  $\{\phi\}$  is crucial and we should retain the possibility of the optimization of the localized orbitals  $\{\phi\}$ .

Figure 1 shows the resultant or optimized form of  $\{\phi\}$  on a real-space mesh. It is clear that the initially s-Gaussian orbital keeps the s-symmetry in the ground state, while the initially  $p_z$ -Gaussian orbitals are mixed with  $p_x$ - and  $p_y$ - Gaussian orbitals. These behaviors of the localized basis orbitals, with the ultrasoft pseudopotential, are very similar to those shown in the Fig. 2 in Hernández *et al.*,<sup>19)</sup> where the ground state of silicon is calculated with a model local pseudopotential.

In summary, we construct foundations for a fully-selfconsistent 'order-N' scheme, within the FD real-space scheme. The essential foundations are (i) the variational principle with respect to nonorthogonal localized orbitals and (ii) the construction of localized orbitals on real-space regular grids. The former issue is resolved by application of the UM technique to the nonorthogonal basis set and the latter issue is resolved by introducing a window function to localize basis orbitals. The formulation is tested numerically on the ground state of diamond crystal with ultrasoft pseudopotential and shows satisfactory agreement with the conventional method.

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