

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 46, NUMBER 12

15 SEPTEMBER 1992-II

Mixed-basis pseudopotential method applied to iterative diagonalization techniques

Andrew M. Rappe

*Department of Physics and Research Laboratory of Electronics,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

A. Dal Pino, Jr.

*Department of Physics and Research Laboratory of Electronics,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
and Instituto Tecnológico da Aeronáutica, São Jose dos Campos, São Paulo 12225, Brazil*

Mark Needels

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

J. D. Joannopoulos

*Department of Physics and Research Laboratory of Electronics,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

(Received 19 March 1992; revised manuscript received 5 May 1992)

We apply a mixed-basis formulation of pseudopotential total-energy electronic structure calculations in the context of iterative diagonalization techniques. The formulation combines a small set of auxiliary functions to describe the localized part of the wave function with a plane-wave basis set. The method is tested on low-symmetry configurations of interstitial oxygen in silicon. This method provides accuracy comparable to plane-wave basis-set calculations and requires less computational effort. Therefore, it appears to be a promising tool for the description of the electronic structure of systems with localized valence electrons.

I. INTRODUCTION

Over the past several years pseudopotential theory has proven to be a powerful approach for the study of the electronic properties¹ of polyatomic systems. An effective and powerful way of applying the pseudopotential method to real materials is to combine it with the supercell approximation and to expand the electronic wave functions in a plane-wave basis set. However, this method is seriously challenged when it is applied to elements which have strongly localized components² of the valence charge density. First-row elements and noble metals are the most salient examples of these elements. The valence pseudopotentials of these atoms are very strong, making it difficult to represent the pseudo-wavefunctions using the conventional plane-wave expansion. The stronger the pseudopotential, the larger the plane-wave basis set has to be. In spite of the introduction of new iterative methods³⁻⁵ and pseudopotentials⁶⁻⁹ that possess optimum convergence in plane waves, this procedure is computationally very demanding.

On the other hand, if one can view the solid-state wave

function as only a small perturbation from a periodic array of overlapping atomic wave functions, then a basis set consisting of a few atomic orbitals would be an efficient spanning set for the solid-state wave function. Unfortunately, this is often not the case. If a purely localized orbital basis is used, one normally finds that several orbitals from excited atomic states are needed to give a reasonable description of the charge density.

It is clear that an approach which combines localized functions and plane waves in the basis set has the potential to overcome these difficulties. However, previous applications^{10,11} of mixed-basis methods have shown that they possess challenging features of their own, which include manipulating more complicated forms for the basis functions and overcompleteness of the basis set. Recently, Jansen, Sankey, and Klein (JSK) (Refs. 12 and 13) have introduced a mixed-basis formalism designed to combine some of the advantages of both pictures. The new feature of their formulation is the use of linear combinations of plane waves as the localized components of the basis set.

In the JSK scheme, the localized orbitals are generated

from pseudoatomic wave functions and subsequently expanded in a plane-wave set which spans a space orthogonal to the space of the plane-wave part of the basis set. Thus, both parts of the basis set (localized and delocalized) are described by plane waves. This eliminates the aforementioned problems of overcompleteness and the basis functions are easy to manipulate. Moreover, the basis set in this approach may be straightforwardly and systematically improved. In this work, we apply the JSK method to calculations performed with the modern iterative^{3,5} diagonalization techniques and discuss its advantages in those cases where some atoms present strongly localized valence charge densities. As a test, we calculate the migration barrier for interstitial oxygen in silicon (Si:O_i) using both the JSK method and the conventional plane-wave pseudopotential method.

This paper is organized as follows. In the next section, we briefly describe the JSK method and its computational savings when compared to the all plane-wave formulation in the context of iterative diagonalization. Section III compares the electronic structures for low-symmetry configurations of interstitial oxygen in silicon as obtained by mixed-basis and all plane-wave calculations. Finally, in Sec. IV we present our conclusions.

II. COMPUTATIONAL GAINS OF THE MIXED-BASIS METHOD

The JSK method combines most advantages of the conventional plane-wave and mixed-basis pseudopotential approaches. Its first step is to generate N_{loc} localized pseudo-wave-function orbitals $|f'_i\rangle$, for example, from a real-space atomic pseudopotential calculation. A state $|f''_i\rangle$ possessing the discrete translational symmetry of the real-space lattice for the calculation is generated by summing the $|f'_i\rangle$ state over all unit cells. The pseudo-wave-function orbitals $|f''_i\rangle$ are then expressed as linear combinations of plane waves in a large set of N_{pwl} plane waves bounded by a large cutoff E_l . These linear combinations of plane waves are then orthonormalized to the plane waves below a small plane-wave cutoff E_s and to each other, forming the set $|f_i\rangle$. The resulting linear combinations of plane waves are held fixed throughout the electronic relaxation, and they form the localized part of the basis set. To these basis functions is added a set of N_{pws} plane waves, all those below a small cutoff E_s . Therefore, a wave function $|g_{nk}\rangle$ in the new basis can be written

$$\langle \mathbf{r} | g_{nk} \rangle = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{|\mathbf{k}+\mathbf{G}|^2 < E_s} c_{nk\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} + e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{i=1}^{N_{\text{loc}}} d_{nki} \langle \mathbf{r} | f_i \rangle, \quad (1)$$

where

$$\langle \mathbf{r} | f_i \rangle = \sum_{E_s < |\mathbf{k}+\mathbf{G}|^2 < E_l} f_{\mathbf{G}i} e^{i\mathbf{G}\cdot\mathbf{r}}. \quad (2)$$

The unification of traditional mixed-basis and plane-wave pseudopotential methods is evident in this method. The use of the localized basis functions can dramatically

reduce the number of plane waves required. But because the localized functions are fixed finite summations of plane waves, the operations on these functions are as tractable as with plane waves, and orthonormalization of the basis set is extremely simple. This provides a convenient algorithm for systematic improvement of the basis set. As plane waves are added to the plane-wave set by increasing E_s , they are removed from the plane-wave linear combinations which comprise the localized functions. Therefore, *by construction*, the conventional plane-wave pseudopotential method is the limiting case of this method where the energies E_s and E_l are set to be equal.

The simplicity of the basis set also allows this method to take advantage of iterative minimization schemes for electronic and atomic degrees of freedom. In particular, this method can be computationally more efficient than the plane-wave pseudopotential method for a judicious choice of localized functions. For example, the computer memory requirement can be reduced to a large extent. When calculating the electronic eigenstates of a system using this method, it is not necessary to store all N_{pwl} plane-wave coefficients for each of the N_b bands, as is required by the plane-wave method. Here, we need only store the N_{pws} plane-wave coefficients below E_s for each band, and one copy each of the N_{loc} linear combinations of $(N_{\text{pwl}} - N_{\text{pws}})$ plane waves. Thus, the total storage of wave functions requires $N_b^* N_{\text{pwl}}$ in the plane-wave method, while this method only requires $(N_b - N_{\text{loc}}) * N_{\text{pws}} + N_{\text{loc}}^* N_{\text{pwl}}$. For the example in this paper, $N_{\text{pwl}}/N_{\text{pws}}$ is about ten, and N_b/N_{loc} is sixteen, so the wave-function storage can be reduced by a factor of 6 by use of this method. When the number of localized basis functions is nearly as large as the number of bands, a modification of this storage procedure is required to realize memory conservation. When a large number of localized basis functions differ only by a spatial translation, only one member of this set of localized functions need be stored, and the rest can be generated by multiplying the stored function by a phase. With this modification, the storage formulas and savings remain the same, except that N_{loc} represents the number of localized orbitals which cannot be translated into one another.

The CPU requirements are also reduced by use of this method. Two computationally intensive steps in an iterative plane-wave minimization are the Fourier transform and orthogonalization of the wave functions, and both of these steps can be speeded up by the use of the mixed-basis approach. In the conventional plane-wave approach, the wave function in Fourier space does not occupy the entire Fourier-transform grid, and so nearly half of the Fourier-transform time can be eliminated.¹⁴ In this approach, the Fourier transform of the localized part of the basis set is done only once for a given atomic configuration. The plane-wave part of the wave function occupies a much smaller fraction of the Fourier-transform grid than in the conventional method, reducing fast Fourier-transform (FFT) CPU time. In our case, FFT time can be reduced by 25% using the mixed-basis approach. The orthogonalization of the wave functions scales like $N_b^2 * N_{\text{pwl}}$. Adoption of this procedure can

speed up this step significantly. Because the mixed basis is orthonormal, orthogonalization requires only $N_b^{2*}N_{pws}$ steps, reducing orthogonalization time by 90%. In addition, use of this mixed-basis method can result in large computational savings within the Kleinman-Bylander nonlocal pseudopotential¹⁵ portion of the calculation. If the localized basis functions are chosen to be the same as the reference states of the nonlocal potential (which is a very natural choice for many pseudopotential calculations), then no spatial projections need be done in the large plane-wave set.

III. INTERSTITIAL OXYGEN IN SILICON

A critical test of the method is its ability to provide accurate results for systems which involve an atom with a strong pseudopotential in very different environments. The oxygen pseudopotential requires a large plane-wave cutoff to achieve converged results, and oxygen can occupy sites with very different character in a lattice of silicon. Accordingly, we have applied this method to study the adiabatic migration barrier for interstitial oxygen in silicon. This adiabatic barrier is the energy difference between the fully relaxed saddle-point geometry and the equilibrium (bridging) configuration (see Fig. 1).

This difficult problem has been previously investigated¹⁶⁻¹⁸ using the plane-wave pseudopotential method. There, the cutoff energy of the plane-wave basis set was chosen to be 40 Ry in order to ensure excellent convergence of the pseudo-wave-functions of the oxygen atom. Here we demonstrate that the application of the JSK procedure allows us to reduce the plane-wave part of our basis set to only 9 Ry, which is the typical value used with pure silicon in the conventional method.

The localized wave functions were generated as follows: (i) four oxygen pseudo-wave-functions (one *s* and three *p*) were loaded onto the supercell lattice and ex-

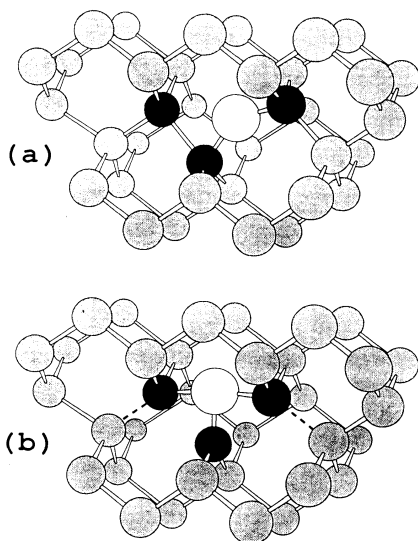


FIG. 1. Atomic configurations of Si:O_i . The open circle represents the oxygen atom and all others correspond to silicon atoms. (a) Stable or bridging configuration. (b) Saddle-point configuration. The dashed lines represent weakened silicon-silicon bonds.

TABLE I. Adiabatic migration barrier energy for Si:O_i .

Method	Plane wave		This work
Cutoff (Ry)	9	40	$E_s=9$ and $E_l=40$
Barrier (eV)	-1.7	1.89	1.84

panded in plane waves up to $E_l=40$ Ry; (ii) these functions were projected out of the space spanned by plane waves up to $E_s=9$ Ry; (iii) finally, the projected functions were orthonormalized and were stored as the local components of our basis set.

This method was then applied to obtain the total energy of the system in both saddle and bridging geometries. For comparison, two conventional plane-wave pseudopotential calculations of the barrier were performed, with 9 and 40 Ry as cutoff energies. For all cases, a 32-atom bcc supercell was used and the *k*-point summations were restricted to the Γ point.

Table I presents the results for the adiabatic migration barrier of Si:O_i as calculated by the mixed-basis procedure and the conventional plane-wave pseudopotential method. We note that there is excellent agreement between the mixed-basis calculation and the conventional plane-wave calculation with the larger cutoff. Moreover, the 9-Ry plane-wave result for the migration barrier differs from the aforementioned results by more than 3.5 eV, and predicts incorrectly that the saddle configuration is more stable than the bridging geometry. Thus, these results demonstrate the ability of the JSK method to reproduce the effect of all plane waves between 9 and 40 Ry at a fraction of the computational cost.

In order to examine in more detail how the mixed-basis and conventional plane-wave calculation compare, we have computed the charge densities of the highest occupied (HO) and lowest unoccupied (LU) states for both geometries. In all cases, the charge densities calculated by the plane-wave method with a 40-Ry cutoff and the mixed-basis method are strikingly similar (see Fig. 2). The charge densities obtained from the 9-Ry plane-wave calculation are very different from the other two calculations for the case of the saddle configuration. This is because the HO and LU states for this geometry have a large amount of oxygen character. On the other hand, the LU and HO states for the bridging configuration are almost entirely siliconlike and are described adequately even with the 9-Ry plane-wave calculation.

IV. CONCLUSIONS

We have applied the JSK mixed-basis pseudopotential approach which uses linear combinations of plane waves as the localized basis functions. The computational savings that can be obtained by this approach were discussed in the context of the new iterative diagonalization techniques. The method was applied to a challenging problem and provided results of similar quality to a well-converged conventional plane-wave pseudopotential calculation, with a considerable reduction of the computational costs. The use of plane waves allows straightforward implementation of iterative minimization schemes. Therefore, we consider this procedure is a very promising tool to study the electronic structure of condensed-matter

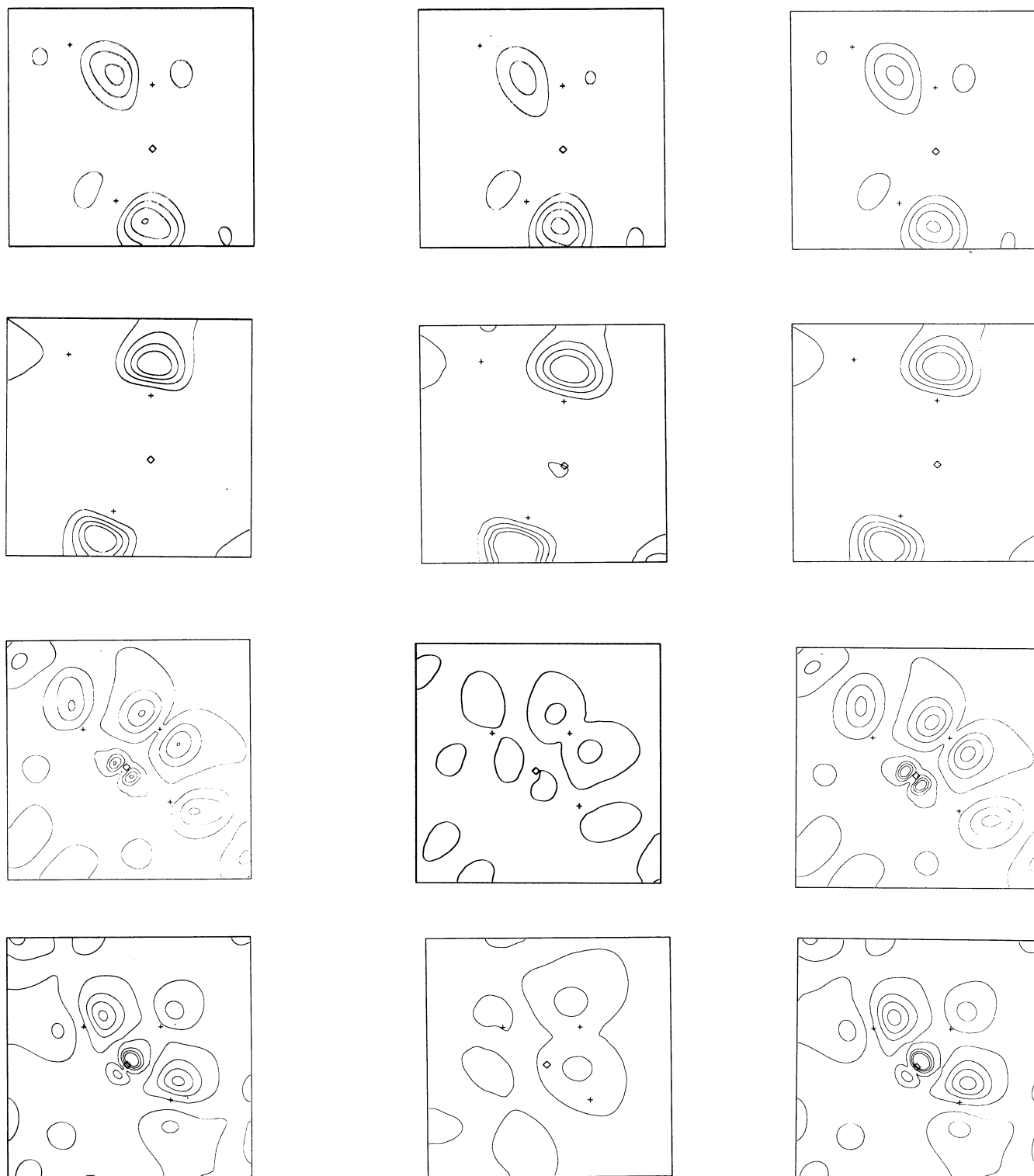


FIG. 2. Contour plot of band charge densities for the Si:O_2 system in the planes defined by the black atoms in Fig. 1. The oxygen atom is represented by a diamond, and the silicon atoms are represented by + signs. Left column: results calculated using 40-Ry plane-wave basis set. Center column: results calculated using 9-Ry plane-wave basis set. Right column: results calculated using 9-Ry/40-Ry mixed-basis set. First row: highest occupied (HO) state in the bridge configuration. Second row: lowest unoccupied (LU) state in the bridge configuration. Third row: HO state in the saddle configuration. Fourth row: LU state in the saddle configuration.

systems with strongly localized components of the charge density.

ACKNOWLEDGMENTS

This work was supported in part by ONR Contract No. N00014-86-K-0158, U.S. JSEP Contract No.

DAAL-03-86-K-0002, and U.S. AFOSR Contract No. 87-0098. A.D.P. is grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil) for financial support. A.M.R. thankfully acknowledges the support of the Joint Services Electronics Program.

¹For recent reviews, see M. L. Cohen, *Phys. Rep.* **110**, 293 (1984); J. D. Joannopoulos, *Physics of Disordered Materials* (Plenum, New York, 1985), p. 19; W. Pickett, *Comput. Phys. Rep.* **9**, 115 (1989), and references therein.

²Y. Bar-Yam, S. T. Pantelides, and J. D. Joannopoulos, *Phys. Rev. B* **39**, 3396 (1989).

³R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

⁴M. P. Teter, M. C. Payne, and D. C. Allan, *Phys. Rev. B* **40**, 12 225 (1989).

⁵M. J. Gillan, *J. Phys. Condens. Matter* **1**, 689 (1989).

⁶A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).

⁷D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

⁸D. C. Allan and M. P. Teter, *J. Am. Ceram. Soc.* **73**, 3247 (1990).

⁹N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

¹⁰S. G. Louie, K.-M. Ho, and M. L. Cohen, *Phys. Rev. B* **19**, 1774 (1979).

¹¹M. H. Kang, R. C. Tatar, E. J. Mele, and P. Soven, *Phys. Rev. B* **35**, 5457 (1987).

¹²R. W. Jansen and O. F. Sankey, *Phys. Rev. B* **36**, 6520 (1987).

¹³R. W. Jansen and M. B. Klein, *J. Phys. Condens. Matter* **1**, 8359 (1989).

¹⁴Z. Levine (private communication).

¹⁵L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).

¹⁶M. Needels, J. D. Joannopoulos, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. B* **43**, 4208 (1991).

¹⁷M. Needels, J. D. Joannopoulos, Y. Bar-Yam, S. T. Pantelides, and R. H. Wolfe, in *Defects in Materials*, edited by P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. L. Weber, MRS Symposia Proceedings No. 209 (Materials Research Society, Pittsburgh, 1991), p. 103.

¹⁸A. Dal Pino, Jr., M. Needels, and J. D. Joannopoulos, *Phys. Rev. B* **45**, 3304 (1992).

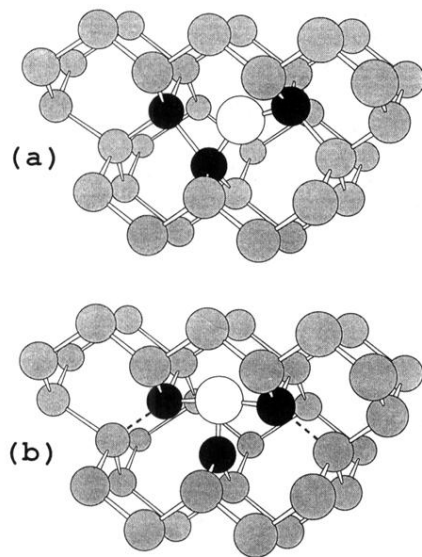


FIG. 1. Atomic configurations of $\text{Si}:\text{O}_7$. The open circle represents the oxygen atom and all others correspond to silicon atoms. (a) Stable or bridging configuration. (b) Saddle-point configuration. The dashed lines represent weakened silicon-silicon bonds.