Direct minimization to generate electronic states with proper occupation numbers

Kikuji Hirose and Tomoya Ono

Department of Precision Science and Technology, Osaka University, Suita, Osaka 565-0871, Japan

We carry out the direct minimization of the energy functional proposed by Mauri, Galli, and Car [Phys. Rev. B **47**, 9973 (1993)] to derive the correct self-consistent ground-state solution of the Kohn-Sham equation. Since this method completely avoids the instability caused by the level crossing, one can determine the electronic structure of metallic systems to a high degree of accuracy without the aid of level broadening of the Fermi-distribution function. The efficiency of the method is illustrated by calculating the ground-state energy of C_2 and Si_2 molecules and the $W(110)$ surface to which a tungsten adatom is adsorbed.

I. INTRODUCTION

In the Kohn-Sham (KS) formulation of density-functional theory,[1,2] the energy functional of a system of electrons is minimum at the point of the ground-state energy with respect to the variation of an arbitrary set of single-particle orthonormal wave functions $\{\psi_i\}$ and occupation numbers $\{n_i\}$. The Janak theorem[2] implies that the occupation numbers of the ground state at zero temperature are chosen such that $n_i=1$ for the states of KS eigenvalues below the Fermi level, and $n_i=0$ for those above the Fermi level. In calculating electronic wave functions, however, constraining the occupation numbers to be integral can frequently cause a convergence difficulty for metallic systems, because a bunch of single-particle states nest in the energy range including the Fermi level and some states move through the Fermi level during the course of self-consistent calculations, i.e., the so-called level crossing happens to occur.[3,4]

One popular approach to prevent this numerical difficulty has been introducing the fractional occupation numbers by using the Fermi-distribution (FD) function with broadening temperature.[4,5] Further, the thermodynamic free energy is minimized instead of the electronic total energy. This procedure has the advantage that the calculations of electronic wave functions for metallic systems typically converge more stably and rapidly, and that the broadening of each level roughly imitates larger systems or a better sampling in the Brillouin zone. In principle, however, no physical significance is given to temperature or entropy in the context of the zero-temperature KS scheme. It is even more serious in practice that theoretical results depend on the chosen values of the fictitious broadening temperature,[6,7] and that one cannot always eliminate this dependence by lowering the temperature down to zero in metallic systems, since the self-consistent cycle frequently enters into the endless loop at low temperature due to the restarting of the level crossing, typical examples of which are found in Refs. 5 and 8.

In this paper, we demonstrate that the direct minimization (DM) of the energy functional proposed by Mauri, Galli and Car (MGC) (Ref. 9) can completely avoid the numerical difficulty caused by the level crossing, and can give satisfactorily the self-consistent solutions of the KS equation without usage of conventional self-consistent field techniques: not only the manifold of the correct-electronic wave functions

but also the proper occupation numbers are numerically determined as output quantities. We combine the DM method with the real-space finite-difference method utilizing the time-saving double-grid technique.[10] The real-space calculation methods have tackled serious drawbacks of the plane-wave approach, e.g., its inability to describe strictly nonperiodic systems such as clusters and solid surfaces.

The rest of this paper is organized as follows: The basic principle of our method is outlined in Sec. II, and the tests which we have performed to probe the usefulness of the scheme are presented in Sec. III. Finally, in Sec. IV we conclude with discussion of future direction for the DM method.

II. MATHMATICAL FORMULATION

The MGC energy functional for an *N*-electron system is written as

$$E[\{\phi\},\eta]=\sum_{\sigma=\uparrow\downarrow}\sum_{i,j}^{M}Q_{ij}^{\sigma}\left\langle\phi_j^{\sigma}\left|-\frac{1}{2}\nabla^2\right|\phi_i^{\sigma}\right\rangle+F[\rho^{\uparrow},\rho^{\downarrow}]$$
$$+\eta\left\{N-\int\rho(\mathbf{r})d\mathbf{r}\right\}, \quad (1)$$

where $\{\phi_i^{\sigma}\}$ is an arbitrary set of *M* linearly independent *overlapping* wave functions with spin index σ, which are assumed here to be real functions for simplicity, and *M* is taken to be not smaller than the number of the occupied states for each spin. $F[\rho^{\uparrow},\rho^{\downarrow}]$ is the sum of the external, Hartree, and exchange-correlation potential-energy functionals, η is the electronic chemical potential, Q^{σ} is an ($M\times M$) matrix: $Q_{ij}^{\sigma}=2\delta_{ij}-S_{ij}^{\sigma}$, and S^{σ} is the overlap matrix: $S_{ij}^{\sigma}=\langle\phi_i^{\sigma}|\phi_j^{\sigma}\rangle$. The charge density is defined as

$$\rho(\mathbf{r})=\sum_{\sigma=\uparrow\downarrow}\rho^{\sigma}(\mathbf{r})\quad\text{and}\quad\rho^{\sigma}(\mathbf{r})=\sum_{i,j}^{M}Q_{ij}^{\sigma}\phi_j^{\sigma}(\mathbf{r})\phi_i^{\sigma}(\mathbf{r}).$$
$$(2)$$

The form of the energy functional Eq. (1) was originally introduced for computation with linear system-size scaling $O(N)$, and each wave function ϕ_i^{σ} was approximated to be a Wannier-like function localized in an appropriate region of space (i.e., a localized orbital) to reduce the amount of com-

putation. In this paper, we adhere to ordinary *extended* wave functions, being free from the errors caused by the localization of wave functions.

$E[\{\phi\}, \eta]$ is minimized by a steepest-descent or conjugate-gradient algorithm *without* constraint of the orthonormalization of wave functions. The derivative of the functional with respect to the function ϕ_i^σ is required for the minimization, which is given by

$$\frac{\delta E[\{\phi\}, \eta]}{\delta \phi_i^\sigma} = 2\sum_j^M \ [(\hat{H}_{KS}^\sigma[\{\phi\}] - \eta)|\phi_j^\sigma\rangle Q_{ji}^\sigma$$

$$- |\phi_j^\sigma\rangle\langle\phi_j^\sigma|(\hat{H}_{KS}^\sigma[\{\phi\}] - \eta)|\phi_i^\sigma\rangle], \quad (3)$$

where $\hat{H}_{KS}^\sigma[\{\phi\}]$ is the KS Hamiltonian. It is straightforward to verify that the ground-state energy is a stationary point of $E[\{\phi\}, \eta]$. Consider the following set of the ground-state wave functions $\{\phi_i^{\sigma 0}\}$: $|\phi_i^{\sigma 0}\rangle = a_i^\sigma|\chi_i^\sigma\rangle$, where $|\chi_i^\sigma\rangle$ is the normalized eigenfunction of $\hat{H}_{KS}^\sigma$ at $\{\phi_i^\sigma\} = \{\phi_i^{\sigma 0}\}$ with the eigenvalue ε_i^σ, i.e., $\hat{H}_{KS}^\sigma[\{\phi_i^{\sigma 0}\}]|\chi_i^\sigma\rangle = \varepsilon_i^\sigma|\chi_i^\sigma\rangle$, and the coefficient a_i^σ is set such that $|a_i^\sigma| = 1$ for $\varepsilon_i^\sigma < \eta$, $0 \leq |a_i^\sigma| \leq 1$ for $\varepsilon_i^\sigma = \eta$, and $a_i^\sigma = 0$ for $\varepsilon_i^\sigma > \eta$. Obviously, $\{\phi_i^{\sigma 0}\}$ is a stationary point of $E[\{\phi\}, \eta]$, since

$$\delta E[\{\phi\}, \eta]/\delta\phi_i^\sigma|_{\{\phi_i^\sigma\} = \{\phi_i^{\sigma 0}\}} = 4a_i^\sigma(1 - |a_i^\sigma|^2)(\varepsilon_i^\sigma - \eta)|\chi_i^\sigma\rangle$$

$$= 0. \quad (4)$$

We now show that the MGC energy functional Eq. (1) is identical to the functional in the standard form

$$E[\{\psi\}, \eta] = \sum_{\sigma=\uparrow\downarrow} \ \sum_i^M \ n_i^\sigma \left\langle \psi_i^\sigma \left| -\frac{1}{2}\nabla^2 \right| \psi_i^\sigma \right\rangle + F[\rho^\uparrow, \rho^\downarrow]$$

$$+ \eta\left\{ N - \int \rho(\mathbf{r})d\mathbf{r} \right\}, \quad (5)$$

with

$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow\downarrow} \rho^\sigma(\mathbf{r}) \quad \text{and} \quad \rho^\sigma(\mathbf{r}) = \sum_i^M n_i^\sigma|\psi_i^\sigma(\mathbf{r})|^2, \quad (6)$$

where $\{\psi_i^\sigma\}$ and $\{n_i^\sigma\}$ are sets of *orthonormal* wave functions and the corresponding occupation numbers, respectively, but n_i^σ varies in the range that $-\infty < n_i^\sigma \leq 1$. The proof is as follows: A set of $\{\phi_i^\sigma\}$ in Eqs. (1) and (2) is transformed to an orthonormal set $\{\tilde{\psi}_i^\sigma\}$ using an orthogonalization algorithm, e.g., the Gram-Schmidt method, and then ϕ_i^σ is represented as $\phi_i^\sigma = \sum_l^M c_{l,i}^\sigma \tilde{\psi}_l^\sigma$. Substituting this expansion into Eqs. (1) and (2), we obtain for the energy functional

$$E[\{\tilde{\psi}\}, \eta] = \sum_{\sigma=\uparrow\downarrow} \ \sum_{k,l}^M P_{kl}^\sigma \left\langle \tilde{\psi}_l^\sigma \left| -\frac{1}{2}\nabla^2 \right| \tilde{\psi}_k^\sigma \right\rangle + F[\rho^\uparrow, \rho^\downarrow]$$

$$+ \eta\left\{ N - \int \rho(\mathbf{r})d\mathbf{r} \right\}, \quad (7)$$

and a similar expression for the charge density, where

$$P_{kl}^\sigma = \sum_{i,j}^M \ Q_{ij}^\sigma c_{k,i}^\sigma c_{l,j}^\sigma = 2T_{kl}^\sigma - \sum_m^M \ T_{km}^\sigma T_{ml}^\sigma, \quad (8)$$

with $T_{kl}^\sigma = \sum_i^M c_{k,i}^\sigma c_{l,i}^\sigma$. Here, the matrix T^σ, of which the element of the k row and the l column is T_{kl}^σ, is a non-negative definite Hermitian matrix, which can be diagonalized by a unitary matrix U^σ as $(U^{\sigma\dagger}T^\sigma U^\sigma)_{kl} = \delta_{kl}\lambda_k^\sigma$ with λ_k^σ being a non-negative eigenvalue of T^σ. Hence,

$$(U^{\sigma\dagger}P^\sigma U^\sigma)_{kl} = \delta_{kl}(2 - \lambda_k^\sigma)\lambda_k^\sigma. \quad (9)$$

Defining ψ_i^σ and n_i^σ as $\psi_i^\sigma = \sum_j^M \tilde{\psi}_j^\sigma U_{ji}^\sigma$ and $n_i^\sigma = (2 - \lambda_i^\sigma)\lambda_i^\sigma$, we obtain Eq. (5) from Eq. (7), and the inequality $-\infty < n_i^\sigma \leq 1$. (Q.E.D.)

This proof gives the way how to define and calculate the occupation numbers $\{n_i^\sigma\}$ within the MGC formalism. One can now recognize that minimizing the MGC energy functional Eq. (1) with respect to $\{\phi_i^\sigma\}$ without imposing the normalization condition is equivalent to treating the occupation numbers $\{n_i^\sigma\}$ as *fractional* occupation variables in the minimization of the functional Eq. (5). It can be also noticed that since the occupation numbers defined above do not exceed one, the Pauli principle automatically works to prevent more than one electron from falling into each single-particle level in the course of the minimization of the the the energy functional Eq. (1). Kim *et al.* showed within a non-self-consistent scheme that the occupation number of the single-particle level below (above) the Fermi level is an asymptote toward one (zero) in the vicinity of the stationary ground-state point of the MGC energy functional.[11] Following this argument, one can easily see that as long as initial wave functions for iterations are chosen to be close to the ground-state solution, the variation range of the occupation number is bounded to $0 \leq n_i^\sigma \leq 1$ and unphysical negative occupation gives rise to no problem in practical calculations. In any case, one should not worry when some occupation numbers are temporarily negative during the minimization process before converging to the stationary point because these occupations do not have a direct physical meaning.

The overall computational scaling in our DM procedure combined with the real-space finite-difference method of Ref. 10 amounts to $O(M^2 N_{grid})$ operations in the calculations of the energy functional Eq. (1) and its derivative Eq. (3), since the ϕ_i^σ's are now assumed to be *extended* wave functions. Here, N_{grid} is the number of coarse grid points in real space. It is noted that $O(M^2 N_{grid})$ is equal to the scaling order in the orthogonalization of wave functions indispensable in the conventional approach of solving the KS equation by an iterative algorithm, and that the dominant scaling in the calculations of the energy functional and its derivative based on a plane-wave basis set is also $O(M^2 N_{basis})$ with N_{basis} being the number of plane-wave basis functions, when advantage is taken of the fast Fourier-transform technique.

III. TEST CALCULATIONS AND DISCUSSION

In order to illustrate the utility of the DM method and the difficulty in the usage of the FD function, the electronic
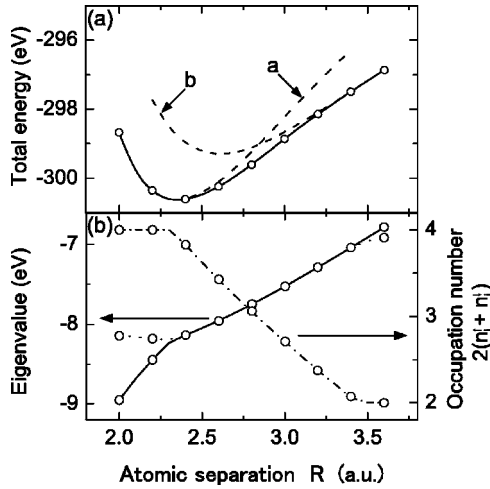
FIG. 1. C_2 adiabatic-potential curve, eigenvalues of $1\pi_u$ and $2\sigma_g$ states, $1\pi_u$ occupancy as a function of atomic separation R. In (a), the solid adiabatic-potential curve is the result with the fractional occupancy by our DM method, and the dashed curves a and b are those with the occupation of the σ_g state constrained to be 0 and 1, respectively. In (b), the solid (dotted) curve represents the eigenvalue of $1\pi_u$ ($2\sigma_g$) state, and the dash-dotted curve shows the occupation number of $1\pi_u$ state. Circles correspond to data obtained by the brute-force method of Ref. 17.

structures of C_2, Si_2, and a tungsten adatom adsorbed on the $W(110)$ surface are calculated. Hereafter, we obey the nine-point finite-difference formula[12] for the derivative arising from the kinetic-energy operator, and the dense-grid spacing is fixed at $h_{dens}=h/3$, where h denotes the coarse-grid spacing.[10] The norm-conserving pseudopotential is employed in a Kleinman-Bylander nonlocal form.[13,14]

We show in Figs. 1 and 2 the results of the application to the carbon dimer as a demonstration of the potential power that our DM method can correctly evaluate both the manifold of the electronic wave functions and the occupation numbers. The carbon dimer is one of the most suitable examples for this purpose, because a number of investigations[3,8,12,15] already showed that the mathematical minimum of the energy functional is with fractional occupations in a certain range of the atomic separation,[16] e.g., Pederson and Jackson[8] found that the fractionally occupied states appear over the range of atomic separation $R=2.4$–3.7 a.u. and the KS eigenvalues of these states are degenerate at the Fermi level. In Figs. 1 and 2, we took the grid spacing $h=0.33$ a.u. in a cell of 16^3 a.u. under the nonperiodic boundary condition (bc) of vanishing wave function, and set the number of electrons $N=8$ and the number of wave functions $M=5$. Exchange-correlation effects were treated with the local-density approximation[17] according to Pederson and Jackson.[8] Figure 1 illustrates the ground-state total energy, the KS eigenvalues of the $1\pi_u$ and $2\sigma_g$ states, and the occupation number of the $1\pi_u$ state as a function of the atomic separation. The result of the brute-force method[15] implementing the manual determination of the occupation numbers is also depicted here in confirmation of the accuracy of our DM method. The results obtained from our DM method accord with those from the other method all over the range of the atomic separation, and
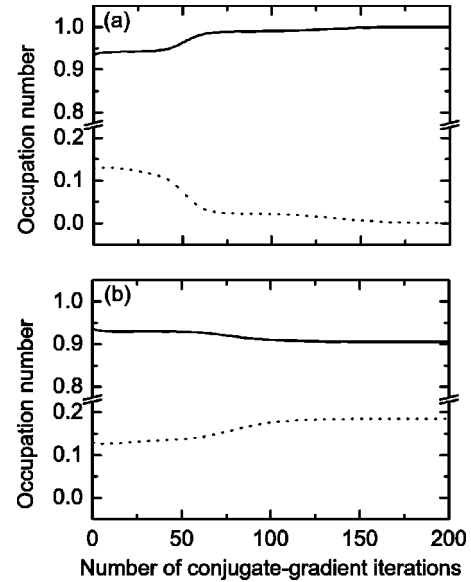

FIG. 2. The occupation number $n_i^\sigma \equiv (2-\lambda_i^\sigma)\lambda_i^\sigma$ as a function of the number of conjugate-gradient iterations. [For the definition of λ_i^σ, see the text preceding Eq. (9).] The solid (dotted) curve represents the occupation numbers of the $1\pi_u$ ($2\sigma_g$) state. The curves in (a) and (b) are the results in the cases of the atomic separation $R=2.30$ a.u. and 2.50 a.u., respectively, and each run starts from the electronic structure at $R=2.40$ a.u.

we can confirm the accuracy and efficiency of our DM method. The calculated equilibrium bond length of the ground-state geometry is $R=2.34$ a.u., being out of the degenerate range, which is in agreement with the experimental value 2.35 a.u. In Fig. 2, we plot the occupation numbers of the states at $R=2.30$ a.u. and 2.50 a.u. as a function of the number of conjugate-gradient iterations, where the electronic structure at $R=2.40$ a.u. is used as the starting point. One can see that the iterative process is markedly stable and our DM procedure gives good convergence of the occupation numbers.

We next give an example that the FD method including a fictitious broadening temperature leads to an incorrect ground-state geometry in molecular-dynamics simulations. Figures 3(a) and 3(b) show the calculated results of the free energy and the force on each atom versus the atomic separation for the silicon dimer, respectively. The calculation was performed under the following conditions: the grid resolution $h=0.50$ a.u., a cell of 24^3 a.u. under the nonperiodic bc and

TABLE I. The diffusion barrier of a tungsten adatom on the rigid $W(110)$ surface along the $[1\bar{1}1]$ direction. Data from our DM method and the FD scheme including a broadening temperature are presented.

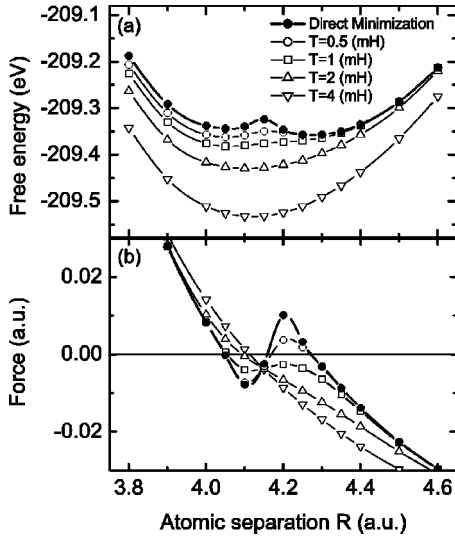| Temperature (mH)	Diffusion barrier (eV)
Present work	1.40
1.0	1.43
2.0	1.54
4.0	1.54

FIG. 3. (a)Si_2 free energy and (b) force on each Si atom as a function of atomic separation R obtained by the DM method and the conventional FD method at different broadening temperatures T. The calculated points are fit to spline-interpolated curves as a guide to the eye. The free energy in the DM method is identical to the total energy. In (b), the force in the FD method is defined as the derivative of the free energy with respect to the atomic position, while the force in the DM method is the true Hellmann-Feynman force defined as the derivative of the total energy.

the local-spin-density approximation[17] for the exchange-correlation potential. The experiments[18] proved that the energy difference between two molecular configurations (i) $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4$ and (ii) $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^2$ that form the double minimum is quite small, the equilibrium bond length is 4.07 a.u. for the configuration (i) and 4.25 a.u. for (ii), and the ground state with the lowest total energy is the latter. Some theoretical analyses have been carried out to examine the situation.[12,15,19] As seen in Fig. 3, our DM procedure can yield results that are in good agreement with the empirical data. On the contrary, the conventional FD method is unable to search out the global minimum configuration (ii) in molecular-dynamics iterations at a broadening temperature $T \gtrsim 1$ mH. At a low temperature $T \simeq 0.5$ mH, the FD method leads to a mistake of regarding the configuration (i) as the ground state with the lowest total energy, although one can find the minimum configuration (ii) by the FD calculations sweeping near the configuration (ii).

As a final example, we evaluate the energy barrier for a tungsten adatom to hop along the $[1\bar{1}1]$ direction on the $W(110)$ surface. Our test system is a cell of 17 tungsten atoms with 102 electrons, consisting of one adatom and two rigid $W(110)$ planes, under the periodic bc at the [001] and $[1\bar{1}0]$ directions, and the nonperiodic bc of vanishing wave function at the [110] one (i.e., thin-film model). The number of wave functions $M = 64$ for each spin, the coarse-grid spacing $h = 0.30$ a.u., and the local-spin-density approximation
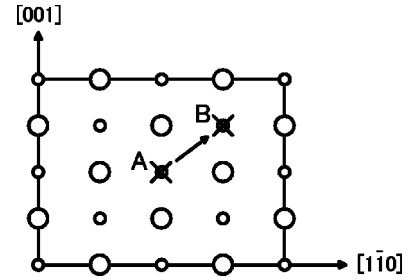

FIG. 4. Top view of $W(110)$ surface-layer atoms (large open circles), second-layer atoms (small open circles) and adatom (crosses) for the surface diffusion discussed in the text.

were employed. Only the Γ point of the Brillouin zone was sampled. Using our DM approach we first evaluate the ground-state geometry for the adatom located at a hollow site A, and then displace the adatom along the $[1\bar{1}1]$ direction from the point A to the nearest hollow site B (see Fig. 4). The diffusion barrier of the tungsten adatom is given in Table I. The numerical error for the barrier at $T = 2$ mH in the FD method is found to be not negligible but about 10% of the true value obtained from our DM scheme. In addition, it is noted that the convergence at $T \leq 1$ mH becomes very slow or diverges in several points on the path AB.

IV. CONCLUSION

We have presented a quite simple and fast algorithm to search out stably the self-consistent ground-state solution as the mathematically well-defined minimum of the energy functional to a high degree of accuracy, and demonstrated that our DM procedure can completely avoid the convergence difficulty caused by the level crossing. Our scheme requires no additional statistical parameter such as a broadening temperature. Since many of those who study the *ab initio* molecular dynamics for metallic systems by using the FD broadening frequently worry about entering into the endless loop of the self-consistent cycle as the broadening temperature goes to zero and have a question for the reliability of the calculation at a finite value of the broadening temperature, our method would be a great blessing to them. Moreover, when a system is assumed to be described in terms of localized wave functions, our procedure makes it possible to perform the calculation with linear system-size scaling $O(N)$. Research in this direction is in progress.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] J.F. Janak, Phys. Rev. B **18**, 7165 (1978).

[3] J. Harris, Phys. Rev. A **29**, 1648 (1984).

[4] G.W. Fernando, G.X. Qian, M. Weinert, and J.W. Davenport, Phys. Rev. B **40**, 7985 (1989); G.X. Qian, M. Weinert, G.W. Fernando, and J.W. Davenport, Phys. Rev. Lett. **64**, 1146 (1990); M. Weinert and J.W. Davenport, Phys. Rev. B **45**, 13 709 (1992).

[5] R.M. Wentzcovitch, J.L. Martins, and P.B. Allen, Phys. Rev. B **45**, 11 372 (1992).

[6] F. Wagner, T. Laloyaux, and M. Scheffler, Phys. Rev. B **57**, 2102 (1998).

[7] M.J. Mehl, Phys. Rev. B **61**, 1654 (2000).

[8] M.R. Pederson and K.A. Jackson, Phys. Rev. B **43**, 7312 (1991).

[9] F. Mauri, G. Galli, and R. Car, Phys. Rev. B **47**, 9973 (1993); F. Mauri and G. Galli, *ibid.* **50**, 4316 (1994).

[10] T. Ono and K. Hirose, Phys. Rev. Lett. **82**, 5016 (1999).

[11] See Fig. 1 in J. Kim, F. Mauri, and G. Galli, Phys. Rev. B **52**, 1640 (1995), in which the variable a_i is connected with the occupation number n_i as $n_i = (2 - a_i^2)a_i^2$.

[12] J.R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72**, 1240 (1994); J.R. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. B **50**, 11 355 (1994).

[13] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[14] We used the norm-conserving pseudopotentials NCPS97 constructed by K. Kobayashi. See K. Kobayashi, Comput. Mater. Sci. **14**, 72 (1999). The inclusion of the nonlocal part of pseudopotentials requires a trivial modification of the energy functional Eq. (1).

[15] B. Dunlap, Phys. Rev. A **29**, 2902 (1984); Chem. Phys. **125**, 89 (1988).

[16] There has been much discussion about the physical significance of fractionally occupied states, e.g., see Ref. 3. From a pragmatic point of view, however, fractional occupation numbers provide the smoothest path to the ground-state geometry as seen in Fig. 1(a).

[17] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

[19] J.E. Northrup, M.T. Yin, and M.L. Cohen, Phys. Rev. A **28**, 1945 (1983).