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### RAPID COMMUNICATIONS

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#### Density-functional molecular dynamics with real-space finite difference

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A real-space scheme based on density-functional molecular dynamics is presented. Two issues are addressed. One is the use of an *exact* finite-difference form of the kinetic-energy operator within a supercell geometry. The second is the introduction of a preconditioning operation in real space. Numerical tests with ultrasoft pseudopotentials show satisfactory accuracy and efficiency of the present real-space scheme.

Car and Parrinello<sup>1</sup> unified molecular dynamics and the electronic density-functional theory<sup>2</sup> under the adiabatic (Born-Oppenheimer) approximation (see Refs. 3 and 4 for review articles). Since then, their method, “density-functional molecular dynamics (DF-MD),” has been applied to various systems, such as solid, liquid, surface, amorphous, and so on. In DF-MD, the adiabatic electronic ground state for a given nuclear configuration is determined by fictitious quenching dynamics with the “force” on wave functions. The most widely used scheme is developed in reciprocal space, called the “dual-fast Fourier transformation (FFT)” scheme,<sup>1,3-5</sup> on the basis of a supercell approximation and a pseudopotential formalism that allow plane-wave expansion of wave functions.

In the dual-FFT scheme, the kinetic-energy part of the wave functions is calculated in reciprocal space. The potential-energy part is calculated from the charge density in real space and then transformed into reciprocal space. For each orbital updating, this procedure requires  $(2N+2)$  routines of fast Fourier transformation, which is dominated by  $O(NM \log M)$  operations and consumes CPU time.<sup>3,4</sup> Here  $N$  is the number of occupied orbitals and  $M$  is the number of bases. Since  $M$  and  $N$  are proportional to the system size or the volume of a bulk system, the operational cost of the  $(2N+2)$  FFT routines is crucial in large systems. Up to now, one can simulate systems containing only about a few hundred atoms in a periodic unit.

In the current scheme of DF-MD, the orthonormality of the wave functions is preserved throughout quenching by Lagrange multipliers. Calculation of the Lagrange multipli-

ers requires  $O(N^3)$  operations and causes another serious problem in the CPU time for simulations in large systems. Mauri *et al.*<sup>6</sup> solved this problem by introducing the “unconstrained minimization” technique, where one can reach the correct ground state without any explicit orthonormalization procedure. Furthermore, they pointed out that their formalism can be applied to large systems with a localization constraint to orbitals.<sup>6</sup>

One of the promising proposals for simulations in large systems is the real-space scheme by Chelikowsky and co-workers,<sup>7,8</sup> where wave functions are defined and updated on real-space equi-interval mesh points and the kinetic-energy operator  $\hat{T}$  is written in a form of real-space finite difference

$$\hat{\phi}_i(\mathbf{r}) = -[\hat{T} + V_{\text{eff}}(\mathbf{r}) - \varepsilon_i] \phi_i(\mathbf{r}) \quad (1)$$

and

$$[\hat{T} \phi_i](\mathbf{r}) \equiv \sum_{\mathbf{r}'} T(\mathbf{r}') \phi_i(\mathbf{r} + \mathbf{r}'), \quad (2)$$

where  $\mathbf{r}$  is a mesh point in real space and  $V_{\text{eff}}(\mathbf{r})$  is a pseudopotential. Chelikowsky and co-workers<sup>7,8</sup> construct a formulation with a fixed boundary condition of vanishing wave functions, but not a periodic boundary condition (supercell approximation). The real-space scheme is advantageous because (i) this scheme can avoid the  $(2N+2)$  FFT routines, the most time-consuming part in the current scheme, and is more amenable to implementation on parallel computing; (ii) it can prepare a local basis set that allows a localization

constraint to orbitals; and (iii) it can be free from a supercell geometry and is applicable to charged or isolated systems.

In this paper, we develop the real-space scheme in two main points; one is a formulation within a supercell geometry. A supercell approximation is good for neutral bulk systems and is advantageous because the Hartree potential can be generated by two FFT routines. In the formulation without a supercell geometry,<sup>7,8</sup> the Hartree potential is obtained by direct integration or numerical solution of the Poisson equation on the real-space grid. The present scheme requires only two FFT routines for each orbital updating and omits the other  $2N$  FFT routines in the current scheme. Furthermore, a supercell approximation leads to an *exact* finite-difference form of the kinetic-energy operator, as explained below. The second point is the introduction of a preconditioning operator

in a form of real-space finite difference so as to accelerate convergence to the ground state.

In the following, we explain in more detail the *exact* finite-difference form of the kinetic-energy operator and the preconditioning operation in real space. Then, numerical tests of the He atom and  $H_2$  molecules with the ultrasoft pseudopotential<sup>9</sup> are performed and show that the present scheme is equivalent to the current dual-FFT scheme in accuracy and the iteration number for convergence.

First, we obtain an *exact* finite-difference form of the kinetic-energy operator within a supercell geometry. Using a pseudopotential formalism, one can assume wave functions to be “soft,” or smoothly varying on real-space equi-interval mesh points. On this assumption, the kinetic-energy operator is exactly written on the mesh points  $(x, y, z)$  in a form of finite difference as

$$\hat{T}\phi(x, y, z) = -\frac{1}{2} \sum_{j=-J}^J f(jh) [\phi(x + jh, y, z) + \phi(x, y + jh, z) + \phi(x, y, z + jh)] \quad (3)$$

and

$$f(x) \equiv -\frac{(g_h^2 - g_L^2) \sin(g_h x)}{\sin(g_L x)} + \frac{2g_L \cos(g_L x) \{g_L \sin(g_h x) \cos(g_L x) - g_h \cos(g_h x) \sin(g_L x)\}}{\sin^3(g_L x)}, \quad (4)$$

where  $h$  is the spacing of the real-space grid,  $L = (2J + 1)h$  is the size of a supercell and  $g_h = \pi/h$  and  $g_L = \pi/L$ . Mesh points in the supercell are denoted as  $jh$  ( $j = -J, -J + 1, \dots, J - 1, J$ ) in one direction. The function  $f(x)$  is the second-order derivative of the function  $F(x)$ ,

$$F(x) \equiv \sum_{j=-J}^J \exp\left(i \frac{2\pi}{L} jx\right) = \frac{\sin(g_h x)}{\sin(g_L x)}, \quad (5)$$

which is the  $\delta$  function on the mesh points. Here we make some comments on this *exact* finite-difference form of the kinetic-energy operator. (i) The number of required mesh points in the summation of Eq. (3) is not  $M = (L/h)^3 = (2J + 1)^3$ , the number of all the three-dimensional mesh points in the supercell, but only  $3M^{1/3}$ . (ii) To clarify the equivalence to the dual-FFT scheme, one can find that this finite-difference form of the kinetic-energy operator is *exact* for wave functions that can be expanded into plane-wave bases with the reciprocal vectors  $\mathbf{g}$ 's where  $|\mathbf{g}| < g_h$ . (iii) The present expression of the kinetic-energy operator does not coincide with that of the usual finite-difference form with  $(2J + 1)$  points, though the higher-order expressions of such finite differences are, numerically, equal to the present expression.

Now turning to the second point, we discuss a preconditioning operation in real space. Since DF-MD performs iterative orbital updates until they reach the ground state, the total CPU time is proportional to the iteration number necessary for convergence. It was pointed out in Ref. 4 that the Kohn-Sham Hamiltonian has high-energy eigenstates, which leads to poor convergence, and that such high-energy eigenstates are nearly plane-wave states. To accelerate conver-

gence, Teter and co-workers<sup>4,13</sup> proposed a “preconditioning” (PC) that reduces erroneous high-momentum (high-energy) components of the force on wave functions and leaves low-momentum components unchanged. Their PC operator is positive definite and diagonal in momentum space. In the dual-FFT scheme, this procedure is done in reciprocal space with a negligible operational cost.

In the real-space scheme, the representation of such a PC operator should be in a finite-difference form. We introduce such an operator  $\hat{P}$  in a form of real-space finite difference

$$[\hat{P}u_i](\mathbf{r}) \equiv \frac{1}{2} \left[ u_i(\mathbf{r}) + \sum_{\mathbf{r}'=h(\pm 1, \pm 1, \pm 1)} \frac{u_i(\mathbf{r} + \mathbf{r}')}{6} \right], \quad (6)$$

where  $u_i(\mathbf{r})$  is the force on the  $i$ th orbital, or the right-hand side of Eq. (1). The second term in the right-hand side of Eq. (6) is the average of the function  $u_i(\mathbf{r})$  on the six nearest mesh points. To see that the operator  $\hat{P}^m$  ( $m$  product of  $\hat{P}$ ;  $m$  is a positive integer) has the required quality of the PC operators, we transform it into momentum space and obtain the representation

$$\hat{P}^m e^{i\mathbf{g} \cdot \mathbf{r}} = \left( \frac{3 + \cos g_x h + \cos g_y h + \cos g_z h}{6} \right)^m e^{i\mathbf{g} \cdot \mathbf{r}}, \quad (7)$$

where  $\mathbf{g} = (g_x, g_y, g_z)$ . This shows that the operator  $\hat{P}^m$  is positive definite for  $-\pi/h < g_x, g_y, g_z < \pi/h$  and diagonal in momentum space. Furthermore, eigenvalues of  $\hat{P}^m$  go to zero once the momenta  $\mathbf{g}$ 's become large. From these properties, the operator  $\hat{P}^m$  prevents the growth of erroneous high-momentum components of wave functions, just as the PC operator in Refs. 4 and 13. In other words, the operator

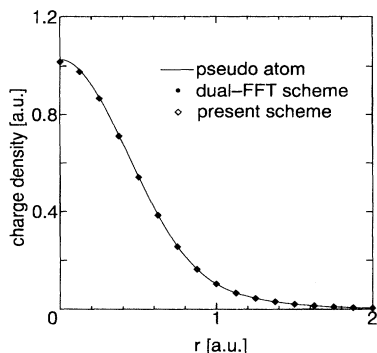


FIG. 1. Charge density of a He atom in real space. We plot the results in the dual-FFT scheme ( $\bullet$ ) and the present scheme ( $\diamond$ ), comparing with a pseudoatom (solid line), a solution of the radial Schrödinger equation on a logarithmic mesh. Note that the plotting data in the two schemes are indistinguishable in the graph.

$\hat{P}^m$  is, essentially, a real-space representation of the PC operator in Refs. 4 and 13. In numerical calculations below, we use the PC operators  $\hat{P}^m$  with  $m = 1, 2, 3, 4, 5, 6$ , where the operation numbers of the PC (at most  $7m$ ) are, though not always negligible, much smaller than that of the kinetic-energy operator ( $3M^{1/3}$ ), because the number of three-dimensional mesh points  $M = (L/h)^3$  is typically of an order of  $100^3$ .

As numerical tests of the present scheme in accuracy and the iteration number for convergence, we calculated the ground state of the He atom and the  $H_2$  molecule. Our calculations are based on the ultrasoft pseudopotential<sup>9,10</sup> and the local-density approximation (LDA) with the Perdew-Zunger exchange-correlation potential.<sup>11</sup> It is only a minor modification to transfer the program from the dual-FFT scheme into the present one, because we can use the same procedures to generate the potential  $V_{\text{eff}}(\mathbf{r})$  from the charge density. One main point of the modification is the kinetic-energy part, as discussed above. Another is that the inner products in the nonlocal, separable pseudopotential are done on the real-space mesh points. We use a cubic supercell with a size of  $L = 8$  a.u. The grid spacing  $h$  is  $h = 0.25$  a.u. or  $h = 0.125$  a.u. For comparison, we also calculate the dual-

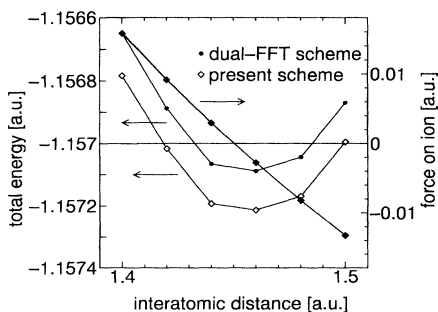


FIG. 2. Total energy and the force on ions of a  $H_2$  molecule as the function of the interatomic distance. We plot the results in the dual-FFT scheme ( $\bullet$ ) and the present scheme ( $\diamond$ ). Note that the plotting data of the forces in the two schemes are indistinguishable in the graph.

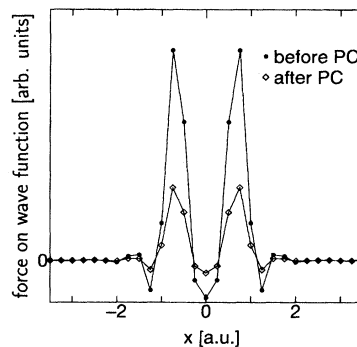


FIG. 3. Force on a wave function of a  $H_2$  molecule in real space in the case of the interatomic distance of 1.4 a.u. We plot the force on wave function before the preconditioning ( $\bullet$ ) and after the (first-order) real-space preconditioning ( $\diamond$ ). Two ions are located at  $x = \pm 0.7$  a.u.

FFT scheme with the same grid spacings. The corresponding “cutoff” energies for wave functions in the dual-FFT scheme are 35 Ry in the case of  $h = 0.25$  a.u. and 100 Ry in the case of  $h = 0.125$  a.u., respectively. It is noteworthy that the two schemes are inequivalent in effective cutoff energy; the dual-FFT scheme requires a cutoff momentum of  $g_c$  for wave functions in reciprocal space and  $2g_c$  for the charge density,<sup>3,4</sup> while the present scheme requires an effective cutoff of  $2g_c$  both for wave functions and for the charge density. So, in a strict sense, the two schemes are equivalent only when the cutoff  $g_c$  is large enough.

In results of the He atom with the grid spacing of  $h = 0.125$  a.u. (equivalent to the cutoff energy of 100 Ry), the total energies of the dual-FFT and the present scheme agree within  $10^{-4}$  a.u. (0.01%). In Fig. 1, we plot the resultant charge density in the dual-FFT and the present scheme and compare them with that of the pseudoatom, a solution of radial Schrödinger equations on a logarithmic mesh. The results in the dual-FFT and the present scheme agree excellently. The agreement not only on the total energy but on the local charge density means that the Hamiltonians in the two schemes are identical and that the finite-difference form in Eq. (3) of the kinetic-energy operator is *exact* in case of soft

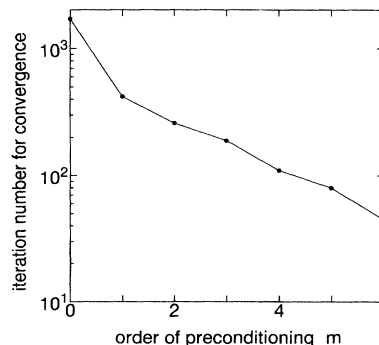


FIG. 4. Iteration number necessary for convergence in the present scheme with the  $m$ th-order preconditioning ( $m = 0, 1, 2, 3, 4, 5, 6$ ). The convergence criterion is  $10^{-5}$  a.u. in the total energy or  $10^{-3}$  a.u. in the force on ions.

wave functions. For the  $H_2$  molecule, we calculate the electronic ground state with some interatomic distances. For both grid spacing  $h=0.25$  and  $0.125$  a.u., the equilibrium interatomic distances in the two schemes are estimated to be between 1.45 and 1.46 a.u., which agrees with other LDA results<sup>12</sup> (1.44–1.45 a.u.). Figure 2 shows the total energies and the forces on ions as the function of interatomic distance with a grid spacing of 0.125 a.u. (equivalent to the cutoff of 100 Ry). We can find, again, an excellent agreement between the results in the two schemes. From the above agreement between the two schemes on the total energy, the local charge density and the forces on ions, we conclude that the present scheme is equivalent to the dual-FFT scheme in accuracy.

As numerical tests for the present real-space PC, we calculate the electronic ground state and the force on ions of the  $H_2$  molecule with an interatomic distance of 1.4 a.u. The calculations are done using the grid spacing of 0.25 a.u. (equivalent to the cutoff of 35 Ry) and the  $m$ th-order PC  $\hat{P}^m$ , where  $m=0,1,2,3,4,5,6$ . The resultant total energies agree within  $10^{-4}$  a.u. (0.01%) for all  $m$ 's. This shows that the present real-space PC does not affect the resultant ground state of the electrons. Figure 3 demonstrates the effect of the real-space PC acting on the force on wave functions; i.e., smoothing and moderating locally in regions near the ions. The iteration numbers to obtain a satisfactory convergence are summarized in Fig. 4, where the criterion for conver-

gence is  $10^{-5}$  a.u. in the total energy or  $10^{-3}$  a.u. in the force on ions. The reduction of the iteration numbers necessary for convergence is remarkable; i.e., the present real-space PC  $\hat{P}^m$  reduces the iteration number from 1500 in the case of  $m=0$  to 45 for  $m=6$ . For comparison, the same calculations are also done in the dual-FFT scheme with the corresponding cutoff (35 Ry) and the resultant iteration numbers for convergence are 150 (without PC) and 20 (with the reciprocal-space PC). From these results, we conclude that the present real-space PC accelerates convergence by a factor of two orders of magnitude and is essential in order to obtain the real-space scheme with a comparable iteration number for convergence to the dual-FFT scheme.

In summary, we develop the real-space scheme of DF-MD in two points. First, we construct a formulation with a supercell geometry and use an *exact* finite-difference form of the kinetic-energy operator. Second, we introduce a PC operation in real space to accelerate convergence to the ground state. Numerical calculations in the present scheme and the current dual-FFT scheme shows that the present scheme is equivalent to the dual-FFT scheme in accuracy and the iteration number for convergence. Furthermore, the present scheme requires only two FFT routines for each iteration.

The numerical calculation was carried out on the NEC SX-3 computer at the Institute of Molecular Science at Okazaki in Japan.

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