APW BASED CAR-PARRINELLO METHOD AND FROZEN PHONON CALCULATION OF SILICON

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ABSTRACT

We examine detailed formulation and numerical accuracy of the augmented-plane-wave based Car-Parrinello method, which has been newly proposed. The method is applied to frozen phonon calculation of Si. The result clearly shows high accuracy and consistency of the method for calculating atomic forces.

Introduction

The Car-Parrinello (CP) method [1] has been widely used for electronic-structure calculations with the density functional theory in the local density approximation. Structural optimization or *ab initio* molecular dynamics simulation can be very efficiently carried out with the CP method since atomic and electronic degrees of freedom are treated on common footing [2].

In almost all calculations with the CP method, plane-wave (PW) functions were taken as the basis set and accordingly pseudopotential (PP) method was adopted. Advantages obtained by using the PW basis set with PP are that atomic force evaluation which is the key ingredient in the CP method becomes much easier since the the PW functions have no dependence on the atomic coordinates and that large numerical errors occurred in the core region can be avoided by removal of the Coulomb singularity. It should be also noticed, however, that there are some serious limitations to use the PW-PP method in its applicability to systems involving spatially localized electronic states or spin polarization.

In the present work, we examine detailed derivation and numerical implication of augmented-plane-wave based Car-Parrinello (APW-CP) method recently proposed by Soler and Williams [3] for overcoming such difficulties. Application of the method to frozen phonon calculation of Si demonstrates high precision and efficiency for the atomic force calculation.

APW based Car-Parrinello Method

The crucial point of the Car-Parrinello method for a practical computation is how one

can get high precision and efficiency in the atomic force calculation. Formulations of the atomic force with use of the APW basis set have been reported quite recently [3-5]. The basic idea of these APW force is essentially equivalent in the sense of evaluating so-called Pulay force which appears as a correction term in addition to well-known Hellmann-Feynman force. But there exist important distinctions among them in the resulting expressions due to a different choice of the APW basis function. We use a modified APW basis set by Soler and Williams [3]. Characteristic feature of Soler-Williams' APW basis set which is different from the conventional APW is that spherical waves (SW) up to the maximum angular momentum, ℓ_{max}, are augmented with muffin-tin (MT) functions inside MT spheres and the higher components remain *unaugmented.* Due to this feature, the wave functions become rigorously continuous in slope and first derivative on the MT spheres. Accordingly, charge density and potential functions can be expressed with a PW representation in the whole space and with a SW one inside the MT spheres. In frozen-augmentation approximation where MT functions remain unchanged by a small atomic displacement, the Pulay force includes only terms due to a change in the continuous condition on the MT spheres, being easily evaluated within the APW formulation.

Frozen Phonon Calculation of Si

The optical phonon frequency of Si at the Γ point was calculated within the frozen phonon approximation to demonstrate accuracy and consistency of the method. A supercell containing two atoms was assumed. Five special points (corresponding to two special points of the original fcc Brillouin zone) for k-space summation and PW cutoff energy of 12Ry were used. Total energies and atomic forces were calculated for slightly displaced atomic positions according to the Γ phonon mode as well as the equilibrium one. The obtained total-energy change, ΔE, and force, F, were fitted to the following functions:

$$\Delta E = \frac{k}{2} u^2 + 4 k_{xyz} \left[\frac{u}{\sqrt{3}} \right]^3, \tag{1}$$

$$F = k\, u + \frac{4}{\sqrt{3}} k_{xyz}\, u^2, \tag{2}$$

where $u = \sqrt{3}\, xa$ is the atomic displacement. Table I shows the force constants, k and k_{xyz}, along with previous theoretical [4,6] and experimental values. Excellent agreement between the values by total-energy and force calculations means consistency of the present APW-CP method. Comparison with experiment in Table I indicates that high accuracy up to the same degree as in the PW-PP calculation can be achieved with the all-electron APW-CP.

Table I Comparisons of k, k_{xyz} and frequency of Γ-point optical phonon in Si calculated from total energy and atomic force with results of FLAPW and PW-PP calculations and experiment.

	k (Ry/a_B)	k_{xyz}(Ry/a_B^3)	f (THz)
Present work			
Total energy	0.5479	0.3726	15.22
Force	0.5481	0.3875	15.22
FLAPW*			
Total energy	0.5586	0.4026	15.37
Force	0.5613	0.4030	15.40
PW-PP+			
Total energy	0.5436	0.357	15.16
Force	0.5422	0.355	15.14
Experiment	0.5704	0.382	15.53

*: reference 4

+: reference 6

Summary

The detailed formulation of the newly proposed APW based Car-Parrinello method was examined and its numerical accuracy was tested by performing a frozen phonon calculation of Si. It was shown that the present method provides very accurate atomic force calculation. The present method does not restrict to elements to be applied as the conventional CP method with PW-PP does. Applications to bulk and surface Cu and other transition metal systems are under way.

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