A Database for Norm-Conserving Pseudopotential (NCPS2K): Application to Rare Gas Atoms

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A norm-conserving pseudopotential database (NCPS95) and updated version NCPS97 have been available since 1995. NCPS97 has been updated to NCPS2K and will be distributed by CD-R media. In the updated version (NCPS2K), new numerical pseudopotential data for the rare gas atoms (He, Ne, Ar, Kr, Xe, Rn) and Ba and At have been prepared. In addition, some pseudopotentials in NCPS97 have been updated and retained. In this database, lattice properties and the absence of ghost bands in the electronic band structures are checked.

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1. Introduction

The plane wave calculation using a pseudopotential is one of the most important methods in electronic structure calculations. The norm-conserving pseudopotential originated by Hamann, Schlüter and Chiang¹⁾ was the first and practical one as the first-principles pseudopotentials. Avoiding core states and smoothed potential curves of valence states, it realized the use of a plane wave basis set in the electronic structure calculation. Using a plane wave basis leads to the easy formulation of forces and stresses. This is an advantage when performing a “Car-Parinello” type first-principles molecular dynamics calculation.

Historically, Bachelet, Hamann and Schlüter (BHS)²⁾ reported a detailed description on how to make the norm-conserving pseudopotential and tabulated parameters of pseudopotentials fitted to analytic functions. Rappe, *et al.*³⁾ and Troullier and Martins (TM)⁴⁾ proposed new soft norm-conserving pseudopotential schemes which realize a reduction in the number of plane waves. Furthermore, a non norm-conserving type pseudopotential scheme appeared as “Ultra-soft pseudopotential” (USPP) devised by Vanderbilt.⁵⁾

One of the most serious problems is unphysical ghost bands which appear when using a separable form as described by Kleinman and Bylander (KB)⁶⁾ in the plane wave pseudopotential calculation. There are no guiding principles by which such a problem can easily be overcome, and trial and error has been necessary. Although some technical approaches for avoiding ghost bands are given in reports,^{7–9)} it requires a knowledge of the electronic structure calculation and how pseudopotentials are made.

The author thought that it would be efficient and useful to prepare a database of norm-conserving pseudopotentials. As a first step, the author constructed the norm-conserving pseudopotential database (NCPS95).¹⁰⁾ The next step was to update NCPS95 to NCPS97.¹¹⁾ At present, NCPS97 is updated to NCPS2K which includes rare gas atoms and Ba and At pseudopotentials.

In this paper, an outline of the pseudopotential database and a calculation method for the electronic structure calculation are described in Section 2. In Section 3, calculated results for

rare gas atoms as a bulk, and Ba and At are presented. Section 4 is devoted to a summary of this study.

2. Method of Calculation

2.1 Outline of pseudopotential database

At present, numerical data for norm-conserving pseudopotentials (over 70 elements in the periodic table) have already been prepared. In this database, it has been checked that there are no ghost bands as a result of the electronic structure calculations up to 1 Ry above the Fermi energy in bulk (bcc, fcc, hcp, *etc.*) by using separable forms.⁶⁾ Logarithmic derivatives for pseudo and real atomic wave functions in some cases have also been checked. A more detailed description is in the author's previous work.^{10,11)}

Two types of numerical data are prepared as for some pseudopotentials which have (shallow) core states (for example: 3d-state of Ga, d-states of rare gas atoms, 3p-state of K, *etc.*). One treats (shallow) core states as valence states, while the other does not treat them in this way. In this study, pseudopotentials for Kr(3d), Xe(4d), Rn(5d), At(5d) treat the core d-states as the valence states.

Most pseudopotentials are constructed with the exchange-correlation of the Wigner interpolation formula.¹²⁾ The exchange-correlation by the Perdew and Zunger type^{13,14)} is used for some pseudopotentials. A scalar relativistic effect¹⁵⁾ without a spin-orbit interaction is considered to these pseudopotentials. Some pseudopotentials are still tentative or being tested at present.

2.2 Electronic structure calculation

The present electronic structure calculation is based on the local (spin) density approximation(L[S]DA)^{12,14,16)} in the density functional theory.^{17,18)} The electronic part is optimized by using the steepest descent type of algorithm which is modified to accelerate convergence of the total energy.¹⁹⁾ In this computer code, it is possible to optimize interatomic coordinates in a unit cell and unit cell shapes using forces and stresses,²⁰⁾ respectively. Therefore, it is possible to perform the structural optimization under a constant pressure condition. Energy cutoff is at 64 Ry, 81 Ry and 100 Ry for most cases. The sampling k-points are 55 (bcc), 89 (fcc) and 95

(hcp) in an irreducible first Brillouin zone (BZ) for bulk.

3. Results and Discussion

3.1 History of calculated systems

A variety of systems have been studied by using NCPS95, -97 , and -2 K and these are listed as follows.

(1) Alkali(Li, Na, K) adsorbed Si(001) surfaces,²¹⁾ (2) SiO₂²²⁾ (High pressure), (3) Hydrogen adsorbed C(001) surfaces,²³⁾

(4) BCN,²⁴⁾ (5) High-pressure phases of Ga^{25,26)} and In,²⁵⁾ (6) Ferromagnetic Fe, Co and Ni,¹⁰⁾ (7) InSb/Sn interfaces,²⁷⁾ (8) High-pressure phase of Tl,¹¹⁾ (9) BN/C interface,²⁸⁾ (10) TiC, ZrC, NbC, HfC, TaC(001) surfaces,²⁹⁾ (11) TiN, ZrN, NbN, HfN, TaN(001) surfaces,³⁰⁾ (12) HfB₂, TaB₂,³¹⁾ WB₂ surfaces, (13) TiB, TiO, TiF(001) surfaces,³²⁾ (14) MgB₂³³⁾ (High pressure), *etc.*

As a result of the present studies, new pseudopotentials of the rare gas atoms (He, Ne, Ar, Kr, Xe, Rn) and Ba and At are

Fig. 1 Energy band structures of rare gas atoms (bulk:fcc). All systems are insulator. "pcc" indicates the partial core correction. "3d", "4d", "5d" indicate the core states.

Fig. 2 Energy band structures of Ba (bcc) and At (fcc). The Fermi level is indicated by the horizontal line. "pcc" indicates the partial core correction. "5d" indicates the core state.

Table 1 Bulk properties (equilibrium lattice constants [nm], bulk moduli [GPa] and deviation[%]). "pcc" indicates the partial core correction. "3d", "4d", "5d" indicate the core states.

	Present work	Exp ³⁵⁾	Deviation
He	0.353 4.22	0.396 1.5 ³⁶⁾	-11
Ne	0.444 2.98	0.446 1.0	-0.45
Ar	0.523 2.4		-1.5
Ar(pcc)	0.530 3.52	0.531 1.6	-0.2
Kr	0.550 5.89		-2.5
Kr(3d,pcc)	0.566 4.52	0.564 1.8	+0.35
Xe	0.599 5.38	0.613	-2.3
Xe(4d,pcc)	0.618 4.36	0.613	+0.8
Xe(theory)		0.619 3.3 ³⁶⁾	-0.2
Rn(pcc)	0.620 5.47		
Rn(5d,pcc)	0.617 6.11		
Ba(bcc,pcc)	0.488 11.3	0.502 10.3	-2.8
At(fcc,pcc)	0.540 33.7		

now available.

3.2 Rare gas atoms (bulk)

As new numerical data for NCPS2K, the pseudopotentials of the rare gases (He, Ne, Ar, Kr, Xe, Rn) are prepared. The author calculates the electronic structures of bulk systems. A calculated structure is a face-centered cubic (fcc). There are three types of pseudopotential: the first treats only outermost s and p states (He, Ne, Ar, Kr, Xe); the second treats outermost s and p states and partial core correction³⁴⁾ (PCC, Ar, Rn); the third treats the outermost core d-states as the valence with PCC (Kr, Xe, Rn). The energy cutoff is 81 Ry for He,

Kr, Xe, and Rn, and 100 Ry for Ar and Ne. The number of k-points is 89 in the irreducible first Brillouin zone. Calculated lattice properties (lattice constant and bulk moduli) are tabulated in Table 1. The calculated lattice constants agree with the experimental values with the exception of He. The values of lattice properties considering the core states as the valence are more accurate than those that exclude the core states. As for the calculated lattice constant of He, the deviation of present and other theoretical³⁶⁾ results is quite large at 11%. Constructing the pseudopotential of He is quite difficult and we were unable to prepare a highly accurate one in this study. Their electronic band structures are shown in Figs. 1(a)–(f). All systems are insulator.

3.3 Calculations for Ba and At

The electronic band structures of Ba and At are calculated. The calculated equilibrium lattice properties are tabulated in Table 1. The lattice constant of Ba found in the present work deviates by 2.8% from that determined in the experiment. There is no data available to compare the At lattice properties which were determined in the present work. The electronic band structures of Ba and At are shown in Figs. 2(a), (b). Ba and At bulk systems are metallic. 5d core states of At are about 30 eV below the Fermi level, which are atomic like flat bands.

Shallow 5p core states of Ba are not incorporated as the valence state in the construction of pseudopotentials in this study. Unoccupied 5d states of Ba are incorporated on the assumption that the 5d states are partially occupied as ionic states in the same way as BHS.²⁾ Hamann³⁷⁾ suggests that it is necessary to consider the 5p core state for Ba compounds.

Although the present Ba pseudopotential is a trial version, and the shorter (-2.8%) lattice constant was carried out, the electronic band structure agrees with the other theoretical result.³⁸⁾

A calculated lattice constant for BaSe in this study is overestimated by about 10% in order to test transferability. Se pseudopotential in NCPS2K has been checked the lattice constants as bulk (fcc: 0.429 nm) and compound (ZnSe: 0.571 nm), which agree with other theoretical (fcc-Se: 0.426³⁶⁾) and experimental (ZnSe: 0.567³⁹⁾) values. It is certain that transferability of Ba pseudopotential in this study is not very good.

4. Summary

The database of norm-conserving pseudopotentials for over 70 kinds of atoms has been constructed. Most of their bulk properties and electronic band structures have been calculated.¹⁰⁾ The next task in constructing this database is to prepare the pseudopotentials of rare-earth elements and modify the pseudopotentials for He and Ba (try to incorporate 5p core states as the valence).

Constructing this database will lead to the prediction (or creating) of new materials, it will also provide support for the synthesis of new experimental materials, help in the search for a new chemical reaction process on surface (catalyst) and solid state characteristics (vacancy, impurity, defect in solid), etc. The final object of this study is to design useful new materials using this database. It is necessary to investigate a greater variety of systems by using NCPS2K in order to realize this object. The author expects that this database will contribute to this approach in the future.

This database (NCPS2K) will be distributed by CD-R media. Detailed information on the database and CD-R distribution are available from the author's web page (the website address is "http://www.nirim.go.jp/staff/kobayak/" or "http://www.geocities.co.jp/Technopolis/4765/").

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