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Theory of *ab initio* pseudopotential calculations

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The *ab initio* norm-conserving pseudopotential is generated from a reference atomic configuration in which the pseudoatomic eigenvalues and wave functions outside the core region agree with the corresponding *ab initio* all-electron results within the density-functional formalism. This paper explains why such pseudopotentials accurately reproduce the all-electron results in both atoms and in multiatomic systems. In particular, a theorem is derived to demonstrate the energy- and perturbation-independent properties of *ab initio* pseudopotentials.

I. INTRODUCTION

Ab initio calculations of the structural properties of solids are of fundamental importance in solid-state physics. These calculations provide a testing ground for well-developed theories such as the local-density-functional (LDF) formalism.[1] A recent successful theoretical study[2] of various structural properties of crystalline Si yields results in excellent agreement with experiment and suggests that theoretical predictions of some unknown structural properties are possible within the LDF formalism. In this paper, we will discuss the *ab initio* pseudopotential approach used in the study. In particular, we give reasons why the pseudopotential approximation, in which the interactions between valence electrons and atomic cores are approximated by appropriate effective pseudopotentials, yields results closely simulating the all-electron results.

Two types of approaches have been developed in *ab initio* calculations: the all-electron approach and the pseudopotential (valence-electron) approach. In the all-electron approach where the eigenvalues and wave functions of all the electrons (including core electrons) are calculated, it has been possible to obtain impressive results[3] for the zero-temperature equation of state of compressed solids within the density-functional formalism. Some of the methods in the all-electron approach, such as the Green's-function method[4] [Korringa-Kohn-Rostoker (KKR)], the augmented-plane-wave method[5] (APW), and the linear muffin-tin orbital method[6] (LMTO), have shape constraints. The spherical averaging procedure of the charge density used in these methods is a good approximation for the study of the equations of state of closed-packed solids. However, for the study of general structural properties in which the angular dependence of the charge density is important for the determination of small total energy differences between rather different structures, the applicability of the spherical averaging procedure is limited. The linear combination of atomic orbitals method[7] (LCAO) has no shape constraints, but often the limited basis set chosen is not sufficient to make accurate structure comparisons. While there are also no shape constraints in the plane-wave method (PW), its usage in the all-electron approach is almost impossible because of the strong oscillation of the wave functions in the core region. This would require too large a basis set to be practical with available computers.

There are two ways to improve these methods for the study of general structural properties. One is to remove the shape constraints in those methods which are limited by their usage. This task is complicated and difficult. Some attempts[8] have been made in this direction. The other is to transform the all-electron Schrödinger equations into effective equations more suitable for the application of the methods containing no shape constraints like the PW method, the LCAO method, or the mixed-basis method[9] using both PW and LCAO basis functions. In particular, it is quite useful to use an effective *ab initio* pseudopotential to simulate the interaction between the valence electrons and the cores (nuclei plus core electrons) such that no core wave functions have to be included explicitly and the valence wave functions no longer have strong oscillations in the core region. This pseudopotential approach has its root in the well-known fact that the valence electrons play the dominant role in chemical bonding and has as its goal the faithful simulation of the all-electron approach. The reason for the ultimate success of this approach can be partly attributed to the observation that the valence and core states are well separated not only in energy but also in real space for many elements.[10]

In addition to the advantages of having to deal with only the valence states and a relatively smooth potential for fast convergence with respect to the basis-function expansion, the pseudopotential approach facilitates a high-precision calculation of the total energy. The structural properties are studied primarily through comparison of small differences between the large total energies of various systems. The total energies should be precise enough to make structural comparisons meaningful. For example, total energies are required to be precise to about 10 mRy per atom for cohesive energies, 1 mRy for equilibrium lattice constants and bulk moduli, and a tenth of 1 mRy for a frozen-phonon calculation of vibrational frequencies. In an all-electron calculation, the total energy is compared to the configuration in which all electrons and nuclei are infinitely separated. A typical value of the calculated total energy for this physical system is of the order of 1000 Ry per atom. In the pseudopotential approach, the total energy is compared to the configuration in which valence electrons and the atomic cores are infinitely separated. A typical value of the calculated total energy is of the order of 10 Ry per atom which is about a factor of 100 smaller than the corresponding energy in the all-electron calculation. As a consequence, it is easier to achieve high precision in the pseudopotential approach.

In the following section, a brief review of the LDF formalism is given. In Sec. III, the *ab initio* pseudopotential theory is presented with emphasis on the accuracy of the pseudopotential approximation in reproducing the all-electron results in both atomic and multiatomic systems. A theorem is derived to demonstrate the energy- and perturbation-independent properties of *ab initio* pseudopotentials. In Sec. IV, some applications of the *ab initio* pseudopotential method are mentioned to demonstrate the usefulness and power of this method.

II. REVIEW OF THE DENSITY-FUNCTIONAL FORMALISM

The adiabatic (Born-Oppenheimer) approximation[11] serves as the starting point for the formalism to follow. In this approximation, the electronic system is assumed to be in the ground state with respect to the instantaneous nuclear positions. The electronic ground-state energy as a function of nuclear positions is then the effective potential for the nuclear motions. Detailed discussions of the approximation can be found in Ref. 12. Using this approximation, we concentrate on the ground-state energy of the electronic system under the influence of an external potential $v(r)$ and the mutual Coulomb repulsion. The external potential is just the superposition of nuclear Coulomb potentials in this all-electron case.

For such a system, a density-functional formalism has been developed. Hohenberg and Kohn[1] show that the ground-state energy is the variation minimum of the energy expression

$$E[\rho]=\int v(\vec{r})\rho(\vec{r})d\vec{r}+F[\rho]\ , \tag{1}$$

where $F[\rho]$ is a universal functional of the electronic density $\rho(\vec{r})$. To facilitate the application of this formalism to real physical systems, Kohn and Sham[1] reformulated the energy expression (Rydberg units are used throughout this paper). We have

$$\begin{aligned}E[\rho]=&\int v(\vec{r})\rho(\vec{r})d\vec{r}\\&+\frac{1}{2}\int\frac{2\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'+T_s[\rho]\\&+E_{\mathrm{xc}}[\rho]\ .\end{aligned} \tag{2}$$

In this expression, $F[\rho]$ is decomposed into three parts: the electronic Coulomb interaction energy, the ground-state kinetic energy $T_s[\rho]$ of a noninteracting electronic system with electronic density $\rho(\vec{r})$, and a remaining part $E_{\mathrm{xc}}[\rho]$ which is conventionally defined as the exchange-correlation energy of an interacting system with density $\rho(\vec{r})$. The next step is to approximate $E_{\mathrm{xc}}[\rho]$ by a local density functional,

$$E_{\mathrm{xc}}[\rho]\cong\int\rho(\vec{r})\epsilon_{\mathrm{xc}}(\rho(\vec{r}))d\vec{r}\ , \tag{3}$$

where $\epsilon_{\mathrm{xc}}(\rho(r))$ is a function of $\rho(\vec{r})$ and may be interpolated from exchange-correlation energies calculated for the systems of an interacting homogeneous electron gas with various densities. Thus, the solving of the variational problem of Eq. (2) can be transformed to the solving of the one-particle Schrödinger equation:

$$[-\nabla^2+v(\vec{r})+V_H(\vec{r})+V_{\mathrm{xc}}(\rho)]\psi(\vec{r})=\epsilon_i\psi_i(\vec{r})\,, \tag{4}$$

where

$$\rho(\vec{r})=\sum_i n_i\,|\,\psi_i(\vec{r})\,|^2 \tag{5}$$

and n_i, ϵ_i, and $\psi_i(r)$ are, respectively, the occupation number, the eigenvalue, and the wave function of the one-electron state *i*. $V_H(r)$ is the electronic Hartree potential,

$$V_H(\vec{r})=\int d\vec{r}\,'\frac{2\rho(\vec{r}\,')}{|\,\vec{r}-\vec{r}\,'\,|}\,, \tag{6}$$

and $V_{\mathrm{xc}}(\rho)$ is the exchange-correlation potential,

$$V_{\mathrm{xc}}(\rho)=\frac{d(\rho\epsilon_{\mathrm{xc}})}{d\rho}\,. \tag{7}$$

In this way, the total energy of the interacting electronic system is obtained:

$$E_{\mathrm{tot}}=\sum_i n_i\int d\vec{r}\,\psi_i^*(\vec{r})(-\nabla^2)\psi_i(\vec{r})+\sum_i n_i\int d\vec{r}\,\psi_i^*(\vec{r})v(\vec{r})\psi_i(\vec{r})+\tfrac{1}{2}\int d\vec{r}\,\rho(\vec{r})V_H(\vec{r})+\int d\vec{r}\,\rho(\vec{r})\epsilon_{\mathrm{xc}}(\rho)\,. \tag{8}$$

Equations (4) and (8) constitute the backbone of the all-electron approach to study the ground-state properties of matter within the LDF formalism. Here we note that Eqs. (4) and (8) are applicable for pseudopotential calculations in which the nuclear Coulomb potentials are replaced by pseudopotentials, and the wave functions, eigenvalues, and occupation numbers refer to valence states only.[10]

III. *AB INITIO* PSEUDOPOTENTIAL METHOD

The pseudopotential method based on the OPW (Ref. 13) idea was first proposed by Phillips and Kleinman[14] (PK). It has served as a theoretical foundation for subsequent successful applications[15] of pseudopotentials to studies of the electronic structures of solids where major emphasis is placed on the energy eigenvalues. In most of these studies, the pseudopotentials are generated by empirically fitting experimental atomic levels or bulk excitation spectra instead of using the PK prescription which involves a repulsive core-orthogonalization term. If the prescription is carried out exactly, the PK approach is equivalent to the all-electron approach.

Schemes for pseudopotential generation following the PK idea have been developed.[16,17] They involve basically two steps: (a) preparation of nodeless pseudo-wave-functions by mixing the all-electron core wave functions into all-electron valence wave functions for an appropriate atomic configuration, and (b) determination of the pseudopotential by inverting the pseudopotential Schrödinger equation which has the prepared wave functions and the corresponding all-electron eigenvalues as its eigensolutions.

While these schemes represent an important advance toward the goal of accurately simulating the all-electron effects with pseudopotentials, they suffer from an important drawback. The use of the PK idea that the pseudo-wave-function is a linear combination of the true wave function and core wave functions causes the pseudo-wave-function and the true wave function to differ by a constant factor outside the core region resulting from the normalization condition. Carrying out an accurate core-orthogonalization procedure for the wave functions in actual calculations is extremely difficult in practice. Significant errors may result from the inaccuracy of the wave functions for the studies of the structural properties of solids through the small differences in total energy between structures.

The core-orthogonalization procedure can, in fact, be avoided by preparing the nodeless pseudo-wave-functions [step (a)] such that they are equal to the corresponding all-electron wave functions outside the core region. This idea has been emphasized in recent pseudopotential generation schemes.[18–22] Despite the use of different methods for the preparation of the nodeless pseudo-wave-functions, these schemes basically require that, *for a particular reference configuration,* the pseudopotential satisfies the conditions that the pseudopotential results agree with the corresponding *ab initio* all electron results not only for (i) the *valence eigenvalues,* but also for (ii) the *valence wave functions* outside the core region (norm conservation[20]). [These two conditions will be referred to as conditions (i) and (ii) henceforth.] It has been demonstrated[23–25] numerically that these norm-conserving pseudopotentials faithfully simulate the all-electron results both for the single-atom and for the multiatomic systems. In the following, we will give analytic reasons for the accurate simulation of the norm-conserving pseudopotentials in (1) the single atom and (2) the multiatomic systems.

A. Single atom

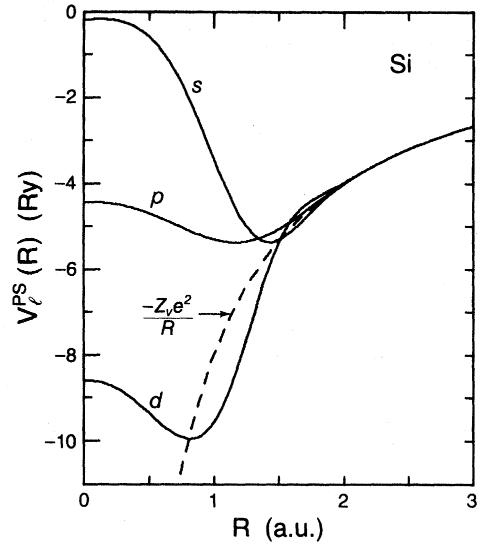

FIG. 1. *Ab initio* core pseudopotential of Si generated (Ref. 20) using the reference configuration of $3s^2 3p^{0.5} 3d^{0.5}$. The letters *s*, *p*, and *d* denote the nonlocal pseudopotential for angular momenta $l=0$, 1, and 2. The dashed line denotes the Coulomb potential of a (fictitious) pointlike atomic core of Si.

We want to show that although conditions (i) and (ii) are required only for a particular reference configuration in the pseudopotential generation, these conditions are also satisfied for a wide range of atomic configurations. In solving the Schrödinger equation for an atomic configuration other than the reference one to self-consistency, we may employ an iteration method. For the initial iterations of both the all-electron (AE) and the pseudopotential (PS) calculations, we adopt the following procedure. Using the occupation numbers of the new configuration and the wave functions $\psi_i(r)$'s of the reference configuration, we obtain the initial guess for the total potential

$$V(r) \equiv v(r) + V_H(r) + V_{\mathrm{xc}}(r)$$

for the new configuration. The difference $\Delta V(r)$ between this initial guess and the self-consistent total potential for the reference configuration may be regarded as a perturbation to the Schrödinger equation of the reference configuration. By perturbation theory, the ith eigenvalue ϵ_i^1 obtained in the first iteration differs from that of the reference configuration by $\Delta\epsilon_i$, where $\Delta\epsilon_i$ is, to the first order in $\Delta V(r)$,

$$\Delta\epsilon_i = \int \psi_i^*(\vec{r}) \Delta V(\vec{r}) \psi_i(\vec{r}) d\vec{r} \ . \tag{9}$$

Let us now compare the corresponding quantities involved in the initial PS interation with those in the initial AE iteration. Since conditions (i) and (ii) are required for the reference configuration in the pseudopotential construction, the corresponding total self-consistent potentials of the reference configuration must agree outside the core region. Because of condition (ii), the corresponding $V(r)$ and

TABLE I. Comparison between the pseudoatomic (PS) and the all-electron (AE) eigenvalues in the self-consistent iterations for the $3s^2 3p^1 3d^1$ configuration of the Si atom. The iteration is initiated with the self-consistent wave functions of the reference configuration ($3s^2 3p^{0.5} 3d^{0.5}$). The results of all-electron frozen-core iterations are denoted by FC's in parentheses.

		Eigenvalues of Si $3s^2 3p^1 3d^1$ (Ry)		
Iteration		3s	3p	3d
First	PS	−0.8479	−0.3558	−0.0078
	AE (FC)	−0.8422	−0.3523	−0.0078
Second	PS	−0.9935	−0.4840	−0.0363
	AE (FC)	−0.9910	−0.4825	−0.0363
Third	PS	−1.0611	−0.5437	−0.0572
	AE (FC)	−1.0596	−0.5428	−0.0572
Self-consistent	PS	−1.0794	−0.5562	−0.0586
	AE (FC)	−1.0780	−0.5552	−0.0586
	AE	−1.0784	−0.5555	−0.0586

TABLE II. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations of Si. Energies are in rydbergs. The method in Ref. 20 is employed to generate the Si pseudopotential using the $3s^2 3p^{0.5} 3d^{0.5}$ reference configuration and Wigner correlation (Ref. 26). The values in parentheses are deviations from the corresponding all-electron results. The Wigner form of exchange-correlation energy is used in (a). No correlation energy is used in (b).

		Eigenvalues		
Configuration	$3s$	$3p$	$3d$	Excitation energy (ΔE_{tot})
(a) Wigner correlation				
$3s^2 3p^2$	-0.7994	-0.3126		0
	(-0.0014)	(-0.0006)		
$3s^1 3p^3$	-0.8538	-0.3543		0.4932
	(-0.0008)	(-0.0004)		(0.0006)
$3s^1 3p^{2.5} 3d^{0.5}$	-1.0226	-0.5048	-0.0380	0.7030
	(-0.0008)	(-0.0006)	(0.0001)	(0.0009)
$3s^2 3p^{0.5} 3d^{0.5}$	-1.4851	-0.9420	-0.3364	0.8774
	(0.0000)	(0.0000)	(0.0000)	(0.0010)
$3s^2 3p^0$	-2.0948	-1.5154		1.7640
	(0.0028)	(0.0024)		(0.0005)
(b) No correlation				
$3s^2 3p^2$	-0.7118	-0.2362		0
	(-0.0016)	(-0.0005)		
$3s^1 3p^3$	-0.7743	-0.2771		0.4906
	(-0.0009)	(-0.0004)		(0.0008)
$3s^2 3p^{0.5} 3d^{0.5}$	-1.4064	-0.8650	0.2731	0.7978
	(-0.0005)	(-0.0002)	(0.0000)	(0.0012)
$3s^2 3p^0$	-2.0055	-1.4294		1.5983
	(0.0021)	(0.0019)		(0.0008)

$\Delta V(r)$ agree outside the core region under the assumption that the valence wave functions do not overlap with the core wave functions appreciably.[10] From Eq. (9), it follows that the corresponding ϵ_i^1's will be very close. The agreement of the corresponding ϵ_i^1's and $V(r)$ outside the core region leads to the agreement of the corresponding resultant wave functions of the first iteration outside the core region.

By repeating the same arguments for subsequent iterations while keeping the AE core orbitals frozen in the reference core orbitals, we find that the eigenvalues and wave functions outside the core region agree quite well iteration by iteration between the AE (frozen core) and the PS cases. Because the core orbitals are well-localized around the nucleus, the subsequent core relaxation in the AE case has little effect on the valence orbitals. Thus, we reach the conclusion that conditions (i) and (ii) are satisfied for the atomic configurations other than the reference one as well.

It also follows from the same reasoning that even if the functional form of the exchange-correlation energy is changed, conditions (i) and (ii) will be satisfied. Thus, the quality of the *ab initio* pseudopotential is, to a large extent, independent of the choice of the reference atomic configuration and the form of the exchange-correlation energy used in the pseudopotential construction as long as conditions (i) and (ii) are satisfied for that particular reference configuration.

Numerical examples for the Si atom are given in Tables I and II. The *ab initio* pseudopotential of Si is generated using the Hamann-Schlüter-Chiang scheme[20] and the Wigner form[26] of the exchange-correlation energy. The reference configuration is chosen to be (Ne core) $3s^2 3p^{0.5} 3d^{0.5}$. The nonlocal *ab initio* pseudopotential is shown in Fig. 1. All three angular momentum components converged to the Coulomb limit rapidly as the radial distance increases. Table I demonstrates the agreement between the PS and the AE (frozen-core) valence eigenvalues in the self-consistent iterations for the $3s^2 3p^1 3d^1$ configuration initiated by the self-consistent wave functions of the reference configuration ($3s^2 3p^{0.5} 3d^{0.5}$). It is interesting to note that the agreement becomes better as the iteration number increases. This is because a large portion of the deviations in eigenvalues of the first iteration comes from the small difference of $\Delta V(r)$ between the AE and the PS cases, which decreases in the self-consistent iterations as a result of electronic screening. The valence eigenvalues of the self-consistent AE calculations with and without the frozen-core restriction are shown in the last two rows of Table I. They differ by less than 1 mRy, which demonstrates that the core-relaxation effects on the valence orbitals are negligible. This point has been discussed in detail in Ref. 27. We note that the frozen-core approximation studied in that paper is different from the pseudopotential frozen-core approximation (or pseudopotential approximation for short) discussed here. In the former approximation, the core states are assumed to be frozen, and the valence states still have strong oscillations in the core region while in the pseudopotential approximation the interaction between the core and the valence electrons is assumed to be frozen and the pseudovalence states are smooth in the core region.

Table II (a) illustrates the good agreement for the eigenvalues and the excitation energies of the pseudoatom with corresponding all-electron results for a wide range of atomic configurations of Si. The relative difference in the wave functions outside the core region between the AE and the PS cases is less than 1% in general. Examples are shown in Fig. 2. As shown in Table II(b), similar agreement is found when only the exchange energy is used for the exchange-correlation energy even though the *ab initio* pseudopotential is generated using the Wigner form of exchange-correlation energy.

B. Multiatomic systems

In solving the Schrödinger equation of a multiatomic system, we may adopt a scattering wave approach and divide real space into an interstitial region and a region consisting of atomic spheres around the atom with a radius R (larger than the core radius) where the total potential is essentially spherically symmetric within R. We solve the Schrödinger equation [Eq. (4)] within the atomic sphere in spherical harmonics and obtain the logarithmic derivatives of the radial solutions as a function of energy ϵ_i on the surfaces of the sphere. These logarithmic derivatives contain all the information about the total potential within the atomic sphere and serve as the boundary condition for the Schrödinger equation in the interstitial region.

We now want to show that for a wide range of energy values these logarithmic derivatives are approximately the same in both the AE and the PS cases. Let us first introduce a theorem: Let $\chi(r)$ and $\chi_1(r)=\chi(r)+\delta\chi(r)$ satisfy, respectively, the radial Schrödinger equations of angular momentum l,

$$\left[-\frac{d^2}{dr^2}+V(r)+\frac{l(l+1)}{r^2}\right]\chi(r)=\epsilon\chi(r)\ , \tag{10}$$

$$\left[-\frac{d^2}{dr^2}+V(r)+\delta V(r)+\frac{l(l+1)}{r^2}\right]\chi_1(r)=(\epsilon+\delta\epsilon)\chi_1(r)\ , \tag{11}$$

for $0\le r\le R$ with the boundary conditions

$$\begin{aligned}&\chi(0)=0\ ,\\&\chi_1(0)=0\ .\end{aligned} \tag{12}$$

It can be shown (see the Appendix) that to first order,

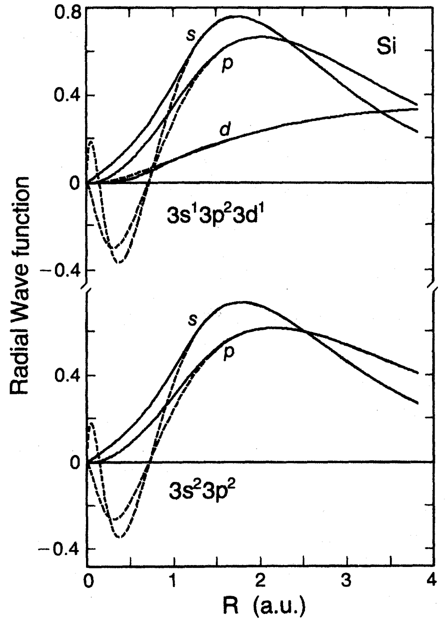

FIG. 2. Comparison between the pseudo- (solid lines) and the corresponding all-electron (dashed lines) radial wave functions for the configurations $3s^1 3p^2 3d^1$ and $3s^2 3p^2$ of Si. The *ab initio* core pseudopotential of Si is generated using the reference configuration of $3s^2 3p^{0.5} 3d^{0.5}$. (See Fig. 1.)

$$\chi^2(R)\delta\left[\frac{\chi'(R)}{\chi(R)}\right]=-\delta\epsilon\int_0^R \chi^2(r)dr + \int_0^R \chi^2(r)\delta V(r)dr \ . \quad (13)$$

An important feature of this theorem is that the change in the logarithmic derivative of the wave function[28] with respect to $\delta\epsilon$ and $\delta V(r)$ depends on the wave function itself and not on $V(r)$ explicitly. Incidentally, by setting $\delta V(r)=0$ in Eq. (13), we obtain

$$\frac{d}{d\epsilon}\left[\frac{\chi'(R)}{\chi(R)}\right]=-\frac{1}{\chi^2(R)}\int_0^R \chi^2(r)dr \ . \quad (14)$$

This equation has been used to demonstrate the energy-independent property of *ab initio* norm-conserving pseudopotentials in Ref. 20, where numerical results were also given to show the agreement of the logarithmic derivatives of the AE and the PS radial functions for a wide range of ϵ's. Equation (13) derived above demonstrates the perturbation-independent property of the pseudopotential in addition to its energy-independent property.

For a multiatomic system, we may again use the iterative method to solve the Schrödinger equation self-consistently. The initial guess of the total potential for the AE (PS) calculation may be constructed from the nuclear Coulomb potential (core pseudopotential) plus the Hartree and exchange-correlation screening potential of a superposition of atomic (valence) charge density of an appropriate neutral atomic configuration. The initial guess of the total potential within the atomic sphere is different from that of the chosen neutral atomic configuration by $\delta V(r)$, which is assumed to be spherically symmetric for simplicity.

Since the wave functions of the chosen atomic configuration agree beyond a certain core radius r_c between the AE and the PS cases, the first term on the right-hand side of Eq. (13) also agrees for $R > r_c$. The same reason related to norm-conserving properties gives that $\delta V(r)$ outside the core region agrees approximately between the PS and the AE cases. In addition, a physical $\delta V(r)$ is slowly varying in the core region and the core region itself is a small portion of the atomic sphere. Therefore, the second term on the right-hand side of Eq. (13) is approximately the same for the AE and the PS cases. It then follows that the logarithmic derivatives (at R) of the radial functions solved from the Schrödinger equation of the first iteration for a range of energy are approximately the same between the AE and the PS cases. This demonstrates that the multiatomic wave functions obtained in the first iteration are approximately the same for the AE and the PS cases.

Using arguments similar to those given in the previous subsection, we show that conditions (i) and (ii) are approximately satisfied for a multiatomic system. This conclusion has been numerically demonstrated by calculating both the AE and the PS electronic structures using the same band-structure methods, for example, the linear APW method[20,23] or the LMTO method.[25] The energy eigenvalues are reproduced to an accuracy of a few hundredths of an eV over a 20-eV range, and the charge density is accurate to a few percent outside the core regions. The PS electronic structures calculated using the mixed-basis method or the plane-wave method also give similar accuracy.[29,30]

At this point we note that the density-functional formalism[1] is developed for the ground-state properties of electronic systems and the energy eigenvalues are only intermediate parameters. The band structure of these eigenvalues cannot be directly used in the interpretation of excitation spectra. For example, the indirect energy gap of crystalline Si is 0.5 eV in both the all-electron[23] and the *ab initio* pseudopotential[2,23] calculations, whereas the experimental value is 1.1 eV. This discrepancy implies that an extended density-functional theory or an entirely new formalism has to be developed to study electronic excitation spectra from first principles.

The above discussions are concentrated on the energy eigenvalues and wave functions. A theorem has been derived[31] stating that the eigenvalues are the derivatives of the total energy with respect to the occupation number of the corresponding orbitals in the LDF formalism. The agreement of the valence eigenvalues over a wide range of atomic configurations for the AE and the PS cases leads to the agreement of the atomic excitation energies defined as the total energy differences between the excited configuration and the ground-state configuration (see Table II). The accuracy of the *ab initio* pseudopotential method in reproducing the all-electron eigenvalues and wave functions outside the core region suggests that similar accuracy may be found in the calculations of total energy changes of a multiatomic system when the chemical environments are changed.

The accuracy of the pseudopotential total energies has been demonstrated in both molecular[24] and crystalline[25] calculations. In the former case, the AE and the PS binding energy curves of the Si_2 dimer calculated using the same LMTO method agree well. In the latter case, both the AE and the PS calculations were carried out for the close-packed phases (bcc, fcc, and hcp) of silicon using the LMTO method. It was found that the pseudopotential approach is quite accurate in reproducing the all-electron volume-dependent total energy curves for the close-packed phases of Si.

C. Applications of the *ab initio* pseudopotential approach

Using the *ab initio* pseudopotential approach, an extensive study[2] of the structural properties has been done for crystalline Si. The same plane-wave band-structure method and the same *ab initio* pseudopotential are used for various aspects of the structural study. Both the qualitative and quantitative results are in excellent agreement with experiment. From a qualitative point of view, among seven possible crystal structures, the theory is able to single out the diamond structure as the most stable phase and the β-tin structure as the final phase when the diamond phase undergoes a pressure-induced solid-solid phase transformation. The quantitative results include the static properties[32] such as the equilibrium lattice constant, bulk modulus, and cohesive energy, the transition volumes and pressure of the diamond-β-tin phase transformation, and the lattice dynamical properties such as the phonon frequencies and mode-Grüneisen parameters at high-symmetry points in the Brillouin zone. In general, the calculated values differ from experiment by only a few percent. Successful structural studies have also been done for other semiconductors such as Se (Ref. 33), Ge (Ref. 34), Sn (Ref. 35), GaAs, and AlAs (Ref. 36), for metals such as Mo and W (Ref. 37) and Al (Ref. 38), and for insulators such as C (Refs. 39 and 40). The overall results are in quite good agreement with experiment despite the material differences.

Besides the structural properties of perfect crystals, the structural properties of defects, impurities, and surfaces represent important and challenging problems. In this kind of structural study, the forces experienced by the individual atoms are useful properties to explore in the search for the most stable structural configurations. The direct calculation of atomic forces can be done through the Hellmann-Feynman theorem.[41] In the all-electron approach, the atomic forces are too sensitive to small errors in the calculation of the core orbitals to be useful in practical calculations. Since the core orbitals have been omitted by the use of the pseudopotential approach, the atomic forces calculated in this *ab initio* method are quite accurate as demonstrated in the Si phonon calculation.[42] Armed with this advantage, a structural reconstruction study[43] of the Si(001)-(2×1) surface has been carried out. A buckled-dimer geometry has been found[44] to be the most stable configuration. Recent experimental evidence[45] strongly favors this geometry. A similar approach has been extended to the spin-polarized version to study the Si(111)-(2×1) surface.[46] An interesting (2×1) antiferromagnetic nonbuckled surface is found to be energetically stable against 2×1 buckling distortions. The bonding geometries of Al deposited on the GaAs(110) surface have also been studied[47] which helps to resolve questions about this chemisorption process.

In view of the studies mentioned above, the *ab initio* pseudopotential theory is an accurate and viable method for the study of the structural properties of solids. It is expected that this technique will be widely used to further the understanding of the structure and cohesion of materials and to predict the properties of structures not yet known experimentally.

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APPENDIX

Using the same notation as in the text, let us consider the integral

$$I=\int_0^R \chi_l(r)\left[\frac{d^2}{dr^2}+\epsilon-V(r)-\frac{l(l+1)}{r^2}\right]\times\chi_l(r)dr\ . \qquad (\mathrm{A1})$$

From Eq. (10), we have to first order in $\delta\chi$,

$$I=\int_0^R \chi(r)\left[\frac{d^2}{dr^2}+\epsilon-V(r)-\frac{l(l+1)}{r^2}\right]\times\delta_{\chi}(r)dr$$

$$=[\chi(r)\delta\chi'(r)-\delta\chi(r)\chi'(r)]\,|_0^R\,. \tag{A2}$$

On one hand it follows from the boundary condition [Eq. (12)] that

$$I=\chi^2(R)\delta\left[\frac{\chi'(R)}{\chi(R)}\right]. \tag{A3}$$

On the other hand, using Eq. (11), Eq. (A1) becomes

$$I=\int_0^R \chi_1(r)[-\delta\epsilon+\delta V(r)]\chi_1(r)dr\,. \tag{A4}$$

Combining Eqs. (A2) and (A4), we have to first order,

$$\chi^2(R)\delta\left[\frac{\chi'(R)}{\chi(R)}\right]=-\delta\epsilon\int_0^R \chi^2(r)dr+\int_0^R \chi^2(r)\delta V(r)dr\,. \tag{A5}$$

We shall mention one minor point in this proof; $\chi(r)$ and $\chi_1(r)$ are determined only to within a multiplicative constant. To make $\delta_{\chi}(r)$ $[\equiv\chi_1(r)-\chi(r)]$ *bona fide* first order, an auxiliary boundary condition should be imposed such as $\chi(R)=\chi_1(R)$ or $\chi_1(r)/\chi(r)=1+O(r)$ for small r. The final result of Eq. (A5), in which the multiplicative constant can be factored out, is independent of the auxiliary boundary condition.

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$$\begin{aligned}\frac{\chi'(R)}{\chi(R)}&=\frac{d}{dr}[\ln\chi(r)]\,|_{r=R}\\&=\frac{1}{R}+\frac{d}{dr}[\ln\phi(r)]\,|_{r=R}\ .\end{aligned}$$

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